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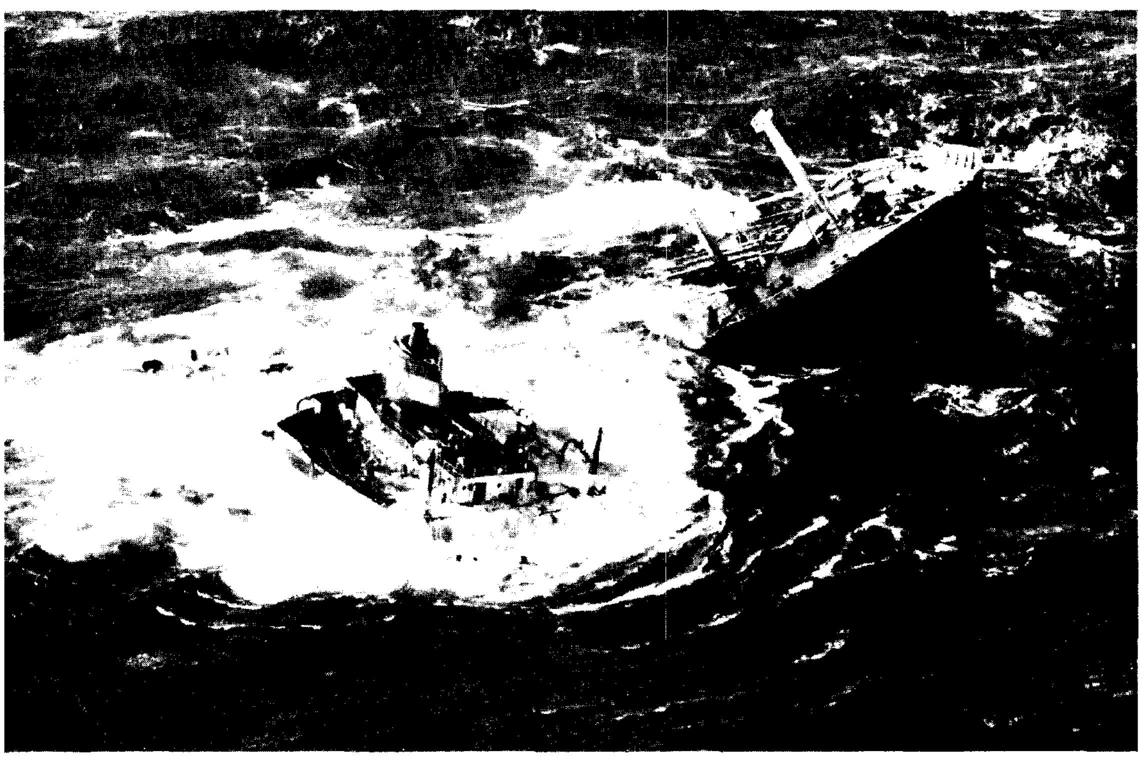
In the Wake of the *Argo Merchant*

Proceedings of a Symposium
Held January 11-13, 1978, at the
Center for Ocean Management Studies,
University of Rhode Island



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The Center for Ocean Management Studies was created in the fall of 1976 for the purpose of promoting effective coastal and ocean management. The Center identifies ocean management issues, holds workshops and conferences to discuss these issues, and develops recommendations and research programs to resolve them.

In the Wake of the *Argo Merchant*

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Center for Ocean Management Studies
University of Rhode Island
August, 1978

Preface

On December 15, 1976, the tanker *Argo Merchant* ran aground southeast of Nantucket Island. The subsequent discharge of its 7,700,000 gallons of No. 6 fuel oil resulted in one of the largest oil spills off the coast of the United States. In response to the spill, researchers from academic institutions and government agencies throughout the country conducted field studies and laboratory experiments to assess the impact of the spill. This document presents the results of those research efforts and summarizes the discussions at a symposium entitled "In the Wake of the *Argo Merchant*" held January 11-13, 1978, at the Center for Ocean Management Studies, University of Rhode Island.

The Center for Ocean Management Studies was created in the fall of 1976 for the purpose of promoting effective coastal and ocean management. It has provided a forum for interdisciplinary communication, research, and education on marine management issues. We believe that the transportation of oil and the threat it poses to the environment is a critical marine issue facing society today. Studies on the physical and chemical fate of oil spills, the biological effects, and the socio-economic impact resulting from people's perceptions will enable us to respond more effectively to future spills and will, we hope, mitigate their impact. In order to achieve this, we must evaluate our research response to a spill such as that of the *Argo Merchant* and discuss the implications of our research results. This is why the Center sponsored the symposium, approximately one year after the spill.

The papers presented in the proceedings of this symposium provide a comprehensive year's documentation of the environmental and socio-economic impacts of the spill. The results of the physical and chemical studies, which were presented on the first day of the symposium, comprise the first two sections of this report. Biological impacts at the site and in surrounding areas were discussed on the second day and are presented in the third section. Following the scientific presentations, disciplinary workshops were held to evaluate laboratory and field techniques and recommend appropriate scientific responses for future spills. The discussions at the workshops are summarized in the session chairman's introduction to each scientific section. The socio-economic impacts of the spill and response plans for future spills were discussed on the last day and are presented in the final sections of this report.

We hope that these proceedings will serve as a historic document and assist various individuals and agencies in responding to future spills.

Acknowledgments

Many people contributed ideas and information to this effort. First and foremost, we would like to thank the members of the Symposium Planning Committee, who developed the program and served as session chairmen:

Dr. Mason Wilson, Professor
Department of Mechanical Engineering and Applied Mechanics
University of Rhode Island

Dr. James Quinn, Professor
Graduate School of Oceanography
University of Rhode Island

Mr. Kenneth Sherman, Director
Narragansett Laboratory
National Marine Fisheries Service

Dr. Paul Lefcourt, National Coordinator
Oil Spill Ecological Damage Assessment
U.S. Environmental Protection Agency

Special recognition must also be given to Dr. Eva J. Hoffman, URI marine research associate, who initiated the idea for a symposium and helped the Planning Committee identify the individuals who had conducted research on the spill. We would also like to thank the researchers, who made this effort possible by pulling together their data and preparing papers.

Numerous individuals at the University provided logistical and technical support in organizing the symposium and preparing the proceedings. However, special recognition must be given to Carol Dryfoos, administrative secretary, Center for Ocean Management Studies, who handled the logistics of the conference and the publication of the proceedings. Vicki Desjardins, URI marine editor, and Peter Brownell, of URI Printing Services, also deserve a special thanks for their combined efforts in the editing and printing of this document.

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Virginia K. Tippie, Executive Director
Center for Ocean Management Studies

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Physical Studies

Mason P. Wilson, Chairman

Summary of Physical Studies

It is the physical and chemical physical processes that control the dispersion of spilt oil into the marine environment. An understanding of these processes is fundamental to almost every aspect of control, cleanup, and environmental assessment of oil spills.

A discussion of these processes and how they affect the nature of the spill and the cleanup operation is presented in the first paper of this session. The second paper lists the chronology of events and describes the character and extent of the oil spill while the third paper presents the results of a series of experiments concerned with the relative velocity of the slick with respect to the surface waters. There are three papers that deal with the forecasting of the movement of the surface slick, one of which also includes subsurface transport. Two types of forecasting (real time and risk type) were presented. A seabed drifter study conducted at the time of the spill showed that bottom transport was similar to that observed by previous investigators. The last paper describes attempts to measure oil dispersed in the water column.

A workshop on physical studies was held following the presentation of the papers to assess our present state of knowledge and understanding of the various physical processes occurring during an oil spill and the present capabilities of forecasting spill movement and behavior.

Spill forecasts are used to (1) aide the OSC in cleanup operations, (2) to help in damage assessment and (3) to establish risks in environmental impact statements. Risk type forecasts based on climatological data, etc., are primarily used in environmental impact statements whereas real time forecasting is relied on by the OSC. There was a great deal of diversity of opinion concerning present capabilities to forecast the motion of a spill; this might in part be due to the diversity of personnel attending the workshop. It was generally agreed that the gross motion of a spill can be predicted with some degree of certainty provided that wind direction and magnitude are accurately forecasted as well as tidal currents. Some of the limitations of our present forecasting capabilities are due to:

(i) the lack of good tidal current data for much of the U.S. coastal waters

(ii) lack of information on pancake formation and the inability to forecast slick thickness

(iii) the inability to predict with any degree of certainty the total area covered by oil

(iv) the inability to accurately predict the motion of the slick around obstructions and islands

(v) the inability to predict the amount of entrainment of oil in the water column and sediment.

The recommendation of the workshop was that much more research is needed to understand oil behavior on water and its fate following a spill. Much more documentation must be done on actual spills. It was suggested that Surface Current Measurement Radar might be a useful tool for such work.

There is a great need to obtain more visual data on slick dynamics in the open ocean such as was obtained by the Navy-NOAA team on pancakes from the *Argo Merchant* spill. Better instrumentation is needed to obtain slick thickness measurements to develop prediction models. The overflights were good which aided in making the *Argo Merchant* spill probably the best documented major spill to date, but there was a consensus that better documentation would be needed in the future to obtain an accurate budget of the fate of the oil.

Better documentation and predictive methods on the fate of the oil could greatly improve the efficiency of chemical and biological investigations. It wasn't until well after the spill that the magnitude of sediment turnover was fully appreciated by most investigators. Drs. Eva Hoffman and James Quinn were the only investigators that mentioned it could have a significant impact on the results obtained from sediment samples.

Much of our state of knowledge concerning the physical aspects of an oil spill is contained in the papers that follow and the reader is urged to study them. At the time of this writing, over a year has passed since the *Argo Merchant* went aground. We are not sure where all of the oil went except that it was dispersed in the North Atlantic along with the oil from the *Grand Zenith* and a host of other lesser spills. The large number of tar balls found along the shoreline of southern New England in the spring of 1977 might be an indication of the fate of some of this oil; however, chemical analysis never proved that they came from either of these two ships. Hopefully by now the oil has been consumed in the ocean by processes of which we know very little about.

Mason P. Wilson, Chairman
Physical Studies Session

The Role of Physical Studies Before, During, and After Oil Spills

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Abstract

When oil is spilled on water, an enormous number of processes take place. Those that fall into the category of "physical processes" include: transport by wind, waves, and currents; spreading on the surface; dispersion into the sea, principally by breaking waves, evaporation and dissolution. The distinction between physical processes and chemical processes cannot be made entirely clear since the effects are often intimately interwoven. Except for mass transport, all of the processes listed above have connections with physical or surface chemistry, although none involve chemical reactions involving molecular changes which are clearly within the domain of chemical processes. When the problem of cleaning up spilled oil is considered, additional physical processes become important. Because spilled oil often forms a thin layer on the surface, effective cleanup requires gathering of the oil with a barrier having a large sweep width. Since the device must have forward motion, we are led to a consideration of the problem of containment of oil by a barrier in a current. The dynamical instability of the oil-water interface is an important consideration and a limitation on sweeping speed. The oil droplets resulting from these instabilities can pass beneath the barrier and result in containment and collection failure. Thus the mechanics of these droplets, including recoalescence with the slick, are of major importance. Substantial study of the various physical processes can be made theoretically, in laboratories, and with relatively small controlled oil spills. These are the studies which we refer to as "studies before oil spills." However, many of the important physical phenomena can only be accurately observed with large quantities of oil in deep water so that the only acceptable way of making the studies is to carry them out during accidental spills and their subsequent associated cleanup efforts. These studies generally point to a lack of sufficient knowledge in certain areas which can then be remedied by studies after a spill or during a subsequent spill. The physical processes which occur after oil is spilled on water are scientifically interesting in their own right and have results which are needed for a determination of the overall effects of an oil spill by combining them with the results of chemical and biological studies. However, there is another role for the scientific community which is often overlooked. The laws of the United States require that the scientific community provide the on-scene coordinator in charge of cleaning up an oil spill with the scientific information he needs to guide him in choosing optimum cleanup technology and logistics. It is important to direct our studies in a way that will achieve that requirement.

Introduction

When oil is spilled on water, a great many processes take place. The categorization of these into physical, chemical, and biological processes is not entirely distinct. For example, the spreading of oil is usually thought of as a physical process, but surface chemistry has been found to play a major role in the spreading process. Similarly, many of the biochemical reactions that take place in living organisms can be considered under both chemical and biological processes. This paper centers on physical processes, but includes some consideration of those aspects of surface chemistry which could also be considered as chemical processes.

The naturally occurring processes that will be considered here which occur when oil is spilled on water are:

(1) Spreading
(2) Mass transport due to:
  (a) wind stress
  (b) water currents due to tides and winds
  (c) waves
(3) Dispersion of oil into the water
(4) Sedimentation
(5) Evaporation
(6) Dissolution

When we try to clean up the spilled oil, other important physical processes come into play. These are:

(1) Seakeeping characteristics of cleanup equipment,

(2) Mass transport due to waves reflected by collection and containment equipment,

(3) Drainage failure of oil booms,

(4) Interfacial oil-water hydrodynamics associated with a layer of oil restrained by a boom above a moving current; a situation which can lead to entrainment of oil droplets into the water which then pass beneath the boom.

It is appropriate to consider why we care about these physical and "weakly chemical" processes. Three reasons for our caring come immediately to mind. First of all, we do not understand some of the physical and chemical effects very well, and as scientists we would like to understand them better. Secondly, the physical and chemical effects influence the fate and environmental impact of the spilled oil. Thirdly, the effects influence the optimum cleanup logistics for any particular oil spill. Each spill with its own oil characteristics and its own external environment will have different optimum cleanup logistics.

The latter two reasons for our caring are recognized by the laws of the United States. The National Oil and Hazardous Substances Pollution Contingency Plan cites the particular relevance of the organization of a standby scientific response capability. From a consideration of the matters considered by that plan, the scientific response capability can be seen to have two major roles:

(1) Advising the on-scene coordinator of the likely course of future events so that optimum response measures can be chosen.

(2) Aiding the Environmental Protection Agency in assessing the damage caused by an oil spill which is a matter required of the EPA.

Here, it is important to point out that assessing the damage of an oil spill does not diminish that damage in any way; whereas optimizing response plans does diminish the ultimate damage. As a result, the role of the scientific community in aiding in the achievement of optimum response measures is the more important role, although it is a role which has not been adequately exercised in the past.

Naturally Occurring Physical Processes

Oil Spreading. The spreading of oil on the sea is a subject which has been under essentially continuous study for the past eight years. During the first part of this period, analytical and laboratory studies dealt with the spread of a liquid having single values of density, viscosity, tension against air, and tension against water. The most well known of these theories is the Fay-Hoult theory (Fay, 1969, and Hoult, 1972). This theory considered a pool of oil of constant volume whose thickness decreased monotonically with distance from the center to the edge. Initially, when the oil was very thick, the theory was based upon a balance between the gravitational spreading forces and the acceleration of the oil and surrounding water. Later, with intermediate oil thicknesses, the theory was based on a balance between the gravitational spreading forces and the viscous retarding forces on the oil slick associated with the boundary layer flow in the water beneath the oil. At the times when the slick was quite thin, the theory was based on a balance between surface tension spreading forces and viscous retarding forces. A number of objections have been cited to the application of this theory to a spreading pool of oil in the sea, even under the idealization of a pool with monotonically decreasing thickness from center to edge. For example, Milgram (1975) has shown that the gravity-viscous phase of the Fay-Hoult spreading must be inapplicable when the boundary layer flow in the water becomes turbulent. The Reynolds numbers of the flow for real oil slicks at sea indicate that this flow must indeed be turbulent. Secondly, he has shown that for many conditions to which the Fay-Hoult gravity-viscous theory has been applied (Offshore Oil Task Group, 1973), the surface tension forces which are neglected actually exceed the gravitational spreading forces. DiPietro and Cox (1975) and Foda and Cox (1977) have shown that even for a single substance, the assumption of single values for oil-water and oil-air tensions is inappropriate. They have shown that at the spreading edge of an oil slick a very thin layer of oil spreads ahead of the bulk region of the slick and have concluded that in this thin layer the spreading pressure, S, varies with position. The spreading pressure is given by:

Figure 1. *A Photograph of Oil Spreading on Water. The oil is opaque so that thick and thin regions can be distinguished by dark and light areas.*
Source: Exxon USA, Third Quarter, 1977, Vol. XVI, No. 3.

$$S = T_{wa} - T_{oa} - T_{ow} \tag{1}$$

where T_{wa} = water-air surface tension
T_{oa} = oil-air surface tension
T_{ow} = oil-water interfacial tension

The force balance for the region of varying spreading pressure is achieved by the shear stress of the water on the oil being equal to the gradient of the spreading pressure.

All of the considerations of spreading described above are for a pool of oil whose thickness decreases monotonically from the center to the edge. However, oil does not generally spread on the sea in this way. An example is shown in Figure 1. As exemplified by the figure, oil often spreads into relatively thick regions (thickness more than 0.5 mm) surrounded by relatively thin regions (thickness less than 0.1 mm). The reason for this phenomenon has been discussed and disputed for years. A postulated, but until recently unproven, reason for the phenomenon was that the slick fractionated into different chemical compositions within the thick regions from those in the thin regions with differences in spreading pressure resulting from the compositional differences. Such a difference in spreading pressure could be balanced by a difference in the gravitational spreading force associated with the observed thickness variation.

An important experiment indicating the possibility of such a fractionation by spreading was reported by Phillips and Groseva (1975). In their experiment, octane, decane, and toluene were mixed to form a "mixed oil". A drop of this mixed oil was placed at the center of an initially clean water surface. The drop spread and samples of the surface were taken at different times and at different distances from the center of the spreading layer. The molar fraction of each type of oil in each sample was determined by gas chromatographic analysis. Fractionation did occur with relatively high molar fractions of toluene and relatively low fractions of decane and octane found far from the center, while higher fractions of decane and octane with lower fractions of toluene were found closer to the center. For the octane-decane-toluene system, toluene is more strongly surface active by comparison with the other constituents. An unrestrained drop of toluene will spread to a layer having a thickness on the order of the molecular dimensions (approximately 20 Angstroms). Disappointingly little information is available about the surface active agents in crude and refined oils.

Recently, the author and Mr. Riyaz Fazal have begun laboratory experiments oriented towards revealing the processes that occur when oil spreads into the characteristic thick and thin regions. In one type of experiment that has been done, a drop containing $1\ \mu\ell$ of oil was allowed to spread in a non-restrained fashion on a surface. The overall extent of spread was determined by first sprinkling talc on the surface and then noting the size of the region from which the talc was pushed away by the spreading oil. By dividing this area into the initial volume of $1\ \mu\ell$, the average oil thickness was obtained. Experiments were done with four different types of crude oil and the spreading was found to stop after a certain area was reached. The average thickness of the oil for each case was: with an Arabian oil called Arabian Light, the thickness was 1110 Angstroms; with an Algerian crude oil called Arzew, the thickness was 2500 Angstroms; with a California oil called THUMS, the thickness was 160 Angstroms; and with a Lybian crude oil called Zuetina, the thickness was 833 Angstroms. Although we do not know the form of the surfactant molecules in these oils, it is certainly unlikely that their molecular dimensions are as large as the observed thicknesses, except possibly for the THUMS. This immediately indicates that the nature of the spreading of crude oil is particularly complicated.

When larger amounts of oil were put on the water surface, the characteristic thick and thin regions were observed. By doing the spreading on water in a film balance (see Figure 2), the spreading pressures could be measured. By varying the location at which oil was put on the surface, it was possible to measure separately the spreading pressure of the thin region against the measurement bar and the thick region against the measurement bar. Differences in spreading pressure were observed. For example, in the case of the Zuetina oil, the spreading pressure of the thick region was found to be 1.5 dynes/cm and that of the thin region to be 2.5 dynes/cm. This indicates that the thin regions can have higher spreading pressures than the thick regions and thereby inhibit the spreading of the thicker regions of oil. The observed difference in spreading pressure of 1 dyne/cm can account for a thickness in the thick regions of 1.5mm, this being of the same order of magnitude as is frequently observed at sea. The spreading pressure variation must result from fractionation of the slick and we

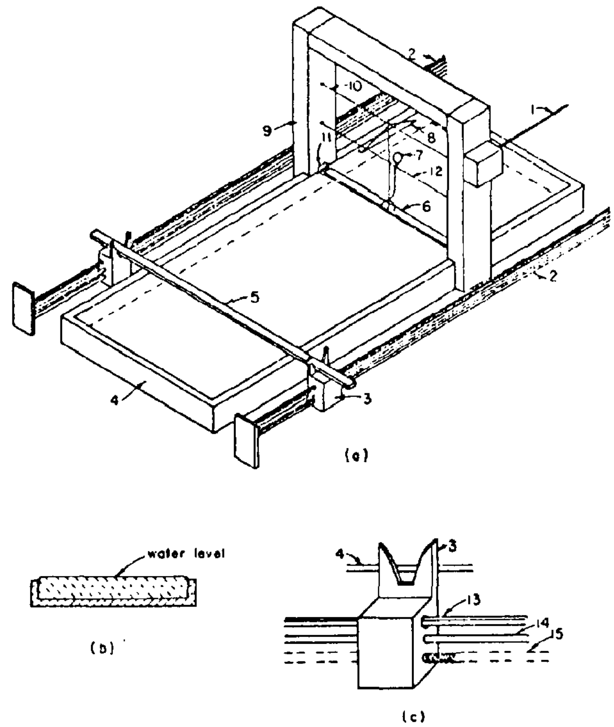


Figure 2. *A Film Balance. 1, torsion wire control; 2, sweep control; 3, sweep holder; 4, trough; 5, sweep; 6, float; 7, mirror; 8, calibration arm; 9, head; 10, torsion wire; 11, gold foil barriers; 12, sighting wire; 13, elevation control; 14, guide; 15, traverse.*
When an oil film floats on the water to the left of the float and the water to the right of the float is clean, the spreading force of the film is exerted on the float. This force is measured by the torsion in the torsion wire needed to hold the float fixed.
Source: Adamson, A. W., Physical Chemistry of Surfaces.

have been able to show conclusively that the fractionation effect observed by Phillips and Groseva in their model system also occurs in crude oil slicks.

Much more remains to be learned about the nature of the oil spreading processes. Important questions about the spreading of the surface active compounds on the water remain unanswered. In particular, we do not know precisely the conditions under which the boundary layer in the water is laminar and those at which it becomes turbulent. Neither do we know the nature of the boundary layer flow in the turbulent region which we must understand in order to be able to predict the shear stress and thereby the ultimate spreading rates. Many of these matters can be understood by theoretical and laboratory studies. However, they must be complimented by field measurements for at least two possible reasons. First of all, if the theoretical and laboratory studies lead to an understanding sufficient for generating a method of predicting how crude oil spreads on the sea, this prediction must be compared with actual measurements in order to assess its accuracy and determine an appropriate confidence level for the predictive capability. Secondly, the analytical and laboratory studies may lead to a semi-empirical theory which requires experimental measurements for determination of certain needed constants. In this case, measurements would be required for some oil spills to determine the constants and for entirely

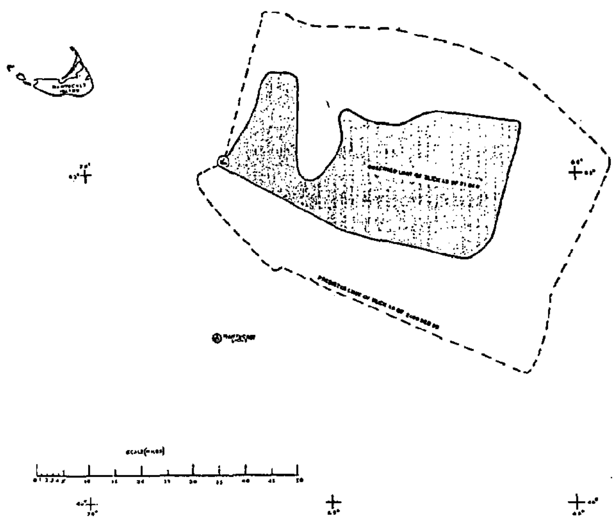


Figure 3. *Comparison of Observed and Predicted Limits of Argo Merchant Oil Slick, Dec. 21, 1977.*
Source: Grose, P. L. and Mattson, J. S. (eds.), The Argo Merchant Oil Spill, A Preliminary Scientific Report.

separate oil spills to check the validity of the resulting predictive capability.

In the case of the *Argo Merchant* spill, the author obtained samples of oil from the thick and thin regions. At that time, and even now, we do not have a predictive capability with which to compare results, nor do we have a semi-empirical theory that can be completed by the addition of field measurements. Nevertheless, it would have been useful to determine if a difference in chemical composition existed between the oil in the thick and thin regions. Such a determination was initially planned. However, the funds to do this work which the EPA had initially indicated would be available did not in fact become available. Thus, we had to cancel plans to do the work because we were unable to pay for it. If we are to gain the information that actual case studies can provide us, it is necessary to have funded plans made in advance.

The Mass Transport of Oil. The prediction of the mass transport of spilled oil, coupled with oil spreading theory, is frequently considered under the topic of oil spill trajectory modeling. An extensive review and bibliography of this subject is given by Stolzenbach, Mattson, Adams, Pollack, and Cooper (1977). Hence, it is not appropriate to delve into the most well known details here, but rather some of the problem areas and some of the recently collected information should be pointed out. Figure 3 shows the observed limits of the *Argo Merchant* oil slick on December 21, 1976 as well as the limit of the slick predicted by a U.S. Coast Guard R&D Center trajectory model (this figure came from Grose and Mattson, 1977). The figure shows that the direction taken by the oil was generally as predicted (downwind) but the area occupied by the slick was only one third of the predicted area (as determined by planimeter measurements of the figure) in spite of the fact that the model apparently did not consider spreading of the oil. If the model considered spreading as well as mass transport, it would have predicted an even larger area.

In the case of the *Argo Merchant* oil spill, the oil went away from shore, a condition for which the combination of the present limits of available cleanup equipment and present knowledge of oil spill effects would indicate that no cleanup actions should be undertaken. If, however, the oil were coming towards shore, cleanup of certain portions of the slick and protection of certain vulnerable coastal areas would have been indicated. Under such a circumstance, it would have been a role of the scientific community to inform the on-scene coordinator of the regions most likely to be impacted by the oil. An error in predicted slick size of a factor of 3 would impose severe restrictions on the applicability of the usefulness of the information that the scientific community could provide.

Obviously, the accuracy of trajectory models can be no better than the basic oil spreading and oil transport information used by the model. It has already been indicated that our ability to predict how oil spreads in a quantitative way is severely limited. However, it has also been pointed out that this is not the reason for the overprediction of the slick area since if spreading were added to the model the area would be overpredicted even more strongly. The mass transport phenomena considered by spill trajectory models are tidal currents, currents due to wind effects on the water, shear stress on the oil imposed by the wind, and the mass transport of the oil caused by the water waves.

Considerable effort has taken place on measuring and then predicting tidal currents in certain areas. For each of these areas, there is an appropriate study which should be undertaken, prior to each tidal measurement program, which is not done in enough cases. This is the study of how the number and location of the tidal measurement stations affects the expected accuracy of oil spill trajectory predictions based on these measurements. Such a study would result in optimization of the tidal data that could be obtained for a fixed amount of funding. With a limited amount of tidal information available, predicting the trajectory of an oil spill can be done in an improved way by utilizing tidal measurements made during and immediately after the spill. Clearly, such information can only be utilized in an effective way if adequate plans for its acquisition and use are made in advance.

The current induced by the direct action of wind over water and the shear stress exerted on oil by wind are subjects about which little experimental information is available. The reason for this is that experiments with wind generate waves which have mass transport of their own that transports the oil. Thus, the motion of the oil in such experiments is affected not only by the water currents directly due to the wind and the shear stress of the wind on the oil, but also by the waves. On the other hand, it is possible to generate waves in a laboratory without wind so wave effects on oil transport can, in principle, be measured. However, since laboratory apparatuses have walls which are not important for waves at sea, and since the size scale in laboratories is necessarily much smaller than the size scale at sea, laboratory experiments cannot be precisely representative of the situation at sea. As a result, most work on the mass transport due to water waves has been done theoretically with specially designed laboratory experiments used for confirming the results. Most of the past work, both theoretical and experimental, was done for depths shallow enough for effects of the bottom to be important.

Until very recently, there was not even a theory suit-

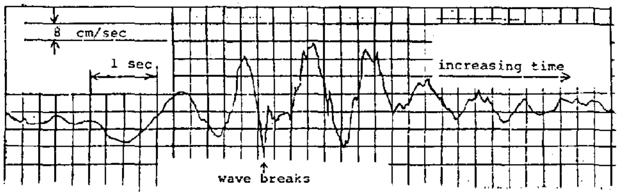


Figure 4. *Horizontal Velocity vs Time Measured at a Fixed Point 2.9 cm Beneath the Mean Free Surface During Passage of a Breaking Wave. The sinuous component of the velocity is due to the underlying wave motion. The jagged component of the velocity is due to the turbulence generated by the breaking process. Turbulent motion results in mixing. The sinuous motion has no mixing. These measurements were made in a laboratory.*

able for the understanding of the mass transport of water without oil for waves in deep water. The theories which had been developed for water of finite depth led to results which were obviously incorrect when the water was deep. Two of these theories which are correct for shallow water are those of Longuet-Higgins (1953) and Unluata and Mei (1970). These theories are applicable to laminar (non-mixing) flows in the water. Recently, the author has considered the problem of mass transport both with and without oil in deep water for laminar (no mixing) flows (Milgram, 1978, I). The result for the mass transport speed at the top of the oil is given by:

$$V = \frac{\sigma^3}{g} A^2 \left(1 + \frac{2\sigma^2\sqrt{\upsilon_w t}}{g\Gamma(3/2)} + \frac{2\sigma^2}{g} + \text{small term}\right) \qquad (2)$$

where

V is the surface fluid flow speed,
σ is the radian frequency of the waves,
A is the wave amplitude (half the height),
g is the acceleration due to gravity,
υ is the kinematic viscosity of the water,
t is the time since the waves first reached the fluid being observed, and
Γ is the gamma function.

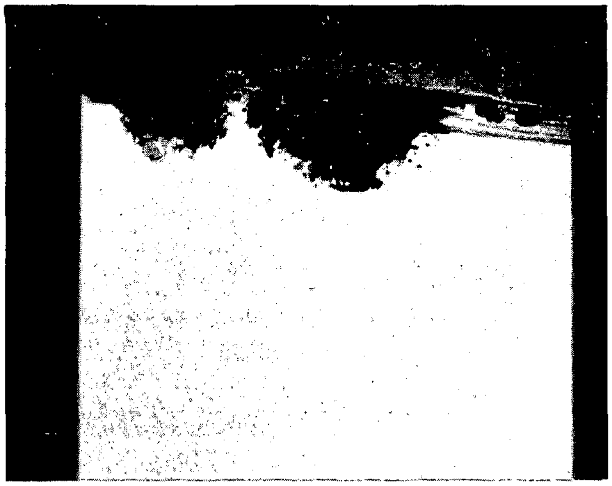
The first term in Equation (2) is the predicted surface transport speed given by Stokes (1947) for an inviscid fluid. Naturally, such a term exists in the water as well. The second term is a slowly increasing term found by the author to be caused by the slow diffusion of vorticity generated at the free surface into the interior of the flow in the water. It exists in the absence of oil as well as in its presence. The third term is the result of the rapid diffusion of surface generated vorticity through the relatively viscous oil. The small term results from non-linear effects in the free surface boundary layer. It involves oil and water densities and viscosities and the oil layer thickness. Its detailed form is given in the reference. The author (Milgram, 1978, II) has performed a series of experiments which confirmed the existence of the third term.

Experiments made by the National Oceanic and Atmospheric Administration, and reported by Grose and Mattson (1977), of oil transport velocities in the *Argo Merchant* oil spill showed oil velocities as much as one percent of the wind speed faster than the velocities of surrounding water. Using typical values for wave heights, wave lengths, oil thicknesses, and wind speeds shows that the third term in Equation (2) is of the same order of magnitude as 1% of the wind speed. The experiments that were done were not detailed enough to determine whether or not it is the third term of Equation (2) that accounts for the incremental oil speed over that of the water measured for the thick layers in the *Argo Merchant* spill. For this particular instance the relative effects of the mass transport term and the shear stress due to the wind are not known well enough to make fully definitive conclusions.

All of the existing theories for mass transport consider laminar flows without mixing. Certainly breaking waves are a source of mixing in the ocean. Figure 4 shows a measurement of the horizontal velocity beneath a breaking wave in the Marine Hydrodynamics Laboratory at MIT. This figure shows turbulent velocities of about one-third the fluid orbital velocities in the waves. However, the turbulent velocities die out very quickly indicating that a fairly rapid succession of breakers would be needed to maintain a significant turbulence level. There is insufficient information available about the near surface turbulence level in the ocean to be able to estimate the effects of natural mixing on the mass transport of oil. Such information is much needed. It can be obtained at sea without oil, but similar studies should be made in the presence of oil since it is known that oil inhibits wave breaking and therefore its presence can diminish the amount of natural mixing. Extrapolating the existing theory without mixing indicates that natural mixing should increase the mass transport of oil due to waves. Thus, the existing theory provides a lower bound on an estimate of the wave induced mass transport velocity.

All commonly used oil spill trajectory models assume a net drift of the oil as some fraction of the wind speed commonly taken as between 2 and 4%. This is to account for the effects of direct wind shear as well as the mass transport due to waves. It is important to distinguish between the two effects since different wind conditions can lead to different waves. For example, in a developing storm with increasing wind speeds the waves will be shorter and steeper than waves for the same wind speed in a diminishing wind after the peak of a storm has passed. Accurate predictions of oil spill trajectories will have to take into account the direct wind shear effects and the wave induced mass transport separately. Much information about determining these effects separately can be found from laboratory experiments coupled with fluid dynamic theory. Since the laboratory scale Reynolds number will necessarily be much smaller than the full scale Reynolds number at sea, direct scaling is impossible. However, it should be possible to develop a semi-empirical theory for the effects with the needed constants determined from careful measurements at sea both with and without oil.

Dispersion of Oil Into the Sea. Observations of oil spills at sea show that when breaking waves interact with floating oil, some of the oil is broken up into small droplets which are driven down deeply into the water. This phenomenon has importance both with regard to control and cleanup measures and with regard to environmental effects of the oil. Since control and cleanup equipment operates at or near the surface, oil which is deeply dispersed cannot generally be contained or collected. Thus, optimum cleanup measures must be based on the anticipated distribution of dispersion. If breaking waves exist in one area but not in another, containment and collection efforts would generally be best concentrated in the area not having breaking waves. On the other hand, if dispersants



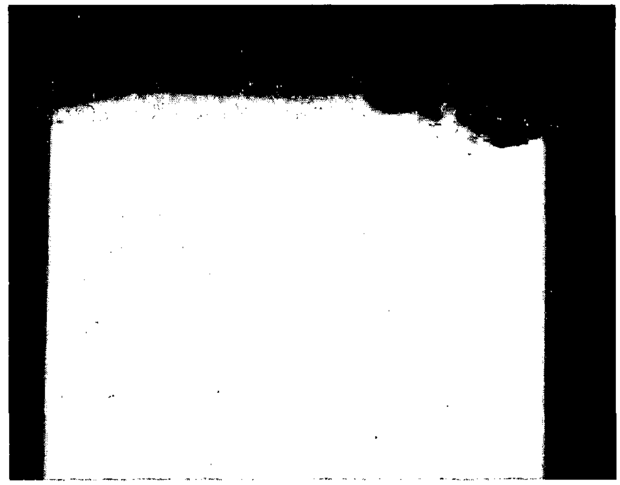


Figure 5. *Photographs of a Breaking Wave Dispersing Oil in a Laboratory Wave Channel.*

(a) The wave breaking has begun at the upper right. The waves go from right to left. The dark gray at the left is the relatively undisturbed oil. The lighter gray beneath it is the far channel window with a layer of oil on it.

(b) The flow in the breaking wave has carried some oil quite deep. Note that on the free surface at the right all the oil is gone and an air-water surface is seen.

(c) The turbulent oil has broken into a cloud of droplets. This is later after the beginning of breaking than the cases shown in the two preceding photographs.

(d) This is after the breaking wave has passed. Many fine droplets remain in the water column. The breaker has opened a "clean" spot on the water surface at the right. The oil that was there has been dispersed into the cloud further to the left.

are to be used, the breaking wave effects can aid in the dispersion and the mixing of the dispersants so areas containing breaking waves might sometimes be the most appropriate ones for application of dispersants.

When there is dispersed oil in the water, there is more surface area of oil available to biological organisms. Whether this is good or bad depends on whether the resulting biodegradation has benefits which outweigh the harm of the poisoning of organisms by the oil or the introduction of the oil into the food chain. In addition, when there are oil droplets in the water, more oil surface is available to suspended sediments which can result in sinking of some of the oil. It is interesting to note that Forrester (1971) found droplets of oil as deep as 80 meters below the surface in Chedapucto Bay weeks after the grounding of the tanker *Arrow.*

Only recently have studies been initiated to determine the details of the mechanism by which breaking waves disperse oil. Figure 5 shows photographs of laboratory experiments of the dispersion by breaking waves phenomenon. In order to be able to make quantitative predictions of dispersion effects for oil spills at sea, much more work is needed. We have found that the sea conditions as well as the oil properties affect the degree of dispersion. Qualitative observations in the field have shown this also. For example, differences in the nature of the dispersion of the oil from the *Argo Merchant* on Nantucket Shoals and the oil from the barge *Ethyl H* in the Hudson River were observed. Both spills were of No. 6 fuel oil. Observation of the oil from the *Argo Merchant* indicated that when it was struck by a breaking wave, it dispersed into the water but soon was seen to rise to the surface again. In the case of the *Ethyl H,* however, following the breaking wave much less rising and recoalescence of the droplets into the slick were observed. No quantitative studies at sea were made during the dispersion process in either case. Such studies would have been quite helpful. Similarly, following the oil spills, laboratory studies of the differences of the oil aimed at determining why the dispersion effects were different would have been quite helpful. Unfortunately, no funds were made available for such studies and they were not carried out.

Sinking and Sedimentation. Very few oils or oil products are heavy enough to sink in sea water. In fact, the only constituents in oil in substantial quantity that by themselves are heavier than sea water are some of the fused aromatic ring compounds and many of these, in fact, float. Thus, unassisted sinking is a rarity.

If heavier-than-water sediments contact the oil, some oil can be absorbed or adsorbed by the sediments with the oil-sediment combination going to the bottom. This can occur either by oil contacting the bottom by escaping from a sunken vessel or by dispersed oil droplets being driven to the bottom by breaking wave turbulence; or by suspended sediments contacting the surface slick or dispersed droplets in the water column.

There is inadequate information available about the conditions and oil type-sediment type combinations that can lead to significant sedimentation. Thus, predictions about sedimentation can only be made in the simplest situations.

Immediately after the *Argo Merchant* began spilling oil, several people pronounced that the damage would be severe because the oil would sink and foul bottom life. These pronouncements were made without any scientific basis.

The author and Dr. Edward Kern took samples of the oil and the water and found that there was no significant quantity of suspended sediment, that oil dispersed by breaking waves appeared to rise rapidly, and that the specific gravity was 0.96 with this figure not changing significantly after the cutter stock was evaporated off. These facts indicated the oil would not sink.

In many spill situations, the evidence will not be so clear. It would be helpful for the on-scene coordinator to know where oil would sink and when this would occur so he could plan optimum cleanup logistics. The planning of surveys to establish damage assessment would benefit from an accurate prediction of sinking distribution. We cannot make accurate predictions of sedimentation in those cases where the correct answer is more obscure than it was in the case of the *Argo Merchant.* Our predictive ability could be improved by studying the problem in laboratories and in the field during and after oil spills.

Evaporation and Dissolution. The evaporation and dissolution of spilled oil is usually considered in the field of chemical studies. However, since these effects are often overlooked, a few words will be devoted to them here.

Table 1 gives the solubilities of the n-paraffins predicted by Parker, Freegarde, and Hatchard (1971). This indicates that dissolution is not significant for paraffins larger than C_{23}. For the smaller molecules, the important factor controlling dissolution is the dissolution rate. The author has found no literature indicating these dissolution rates for oceanic conditions. Laboratory experiments with sea water indicate that in most instances the introduction of oil into the water column by dissolution is negligible in comparison with its introduction by droplet dispersion and by adhering to biological material.

Table 1. Extrapolated Fresh Water Solubilities of n-Paraffins in Heavy Fractions of Crude Oil

Fraction	*Carbon Nos.*	*Extrapolated Solubility in Fresh Water $g.m^{-3}$*
Kerosene	C_{10} - C_{17}	1×10^{-4} - 2×10^{-1}
Gas Oil	C_{16} - C_{25}	6×10^{-4} - 10^{-8}
Lube Oil	C_{23} - C_{37}	10^{-7} - 10^{-14}
Bitumen, etc.	$>C_{37}$	$<10^{-14}$

Source: Parker, Freegarde and Hatchard (1971)

Evaporation can be a major effect in removing oil from the sea. A spill of a relatively volatile oil (including volatile crudes) in warm conditions can easily result in half of the oil entering the atmosphere in a day or two. Prediction of evaporation loss can aid in planning optimum response logistics. Some years ago, some important contributions towards an understanding of the oil evaporation problem appeared in the literature. Blokker (1964) hypothesized a mathematical model for the evaporation of oil in the presence of wind. Blokker did laboratory tests and found his model in poor agreement with measurements for short times and in good agreement for long times. Sivadier and Mikolaj (1973) measured oil loss rates at sea for a small spill of 15 liters of oil and obtained reasonable agreement with Blokker's model. However, they noted the aforementioned thick and thin oil regions in their tests and their measurement methods for determining evaporation rates from slick samples in the non-uniform slick are far from convincing as regards accuracy. No pre-planned quantitative measurements of evaporation rates during large oil spills seem to have been made. Such measurements could be quite helpful in establishing the accuracy of Blokker's model and in pointing the way to more accurate predictive methods if they are needed.

Physical Processes That Occur During Oil Spill Cleanup

Seakeeping Characteristics of Cleanup Equipment. When oil containment and cleanup equipment is used at sea, the characteristics of the motion of the equipment affect the containment and cleanup efficiency. For example, an oil barrier (boom) is of little utility if the oil it is to contain passes over or under the barrier. This will occur if the barrier does not follow the vertical motions of the waves with adequate accuracy. In addition, if a floating barrier does not maintain an essentially vertical fence, but rolls back and forth in the waves to an excessive degree, this rolling motion will allow the oil to pass over or under the barrier. If the barrier does not follow the sway motions of the fluid particles in waves, temporarily high currents between the boom and the water will exist and such currents can draw oil beneath the boom. Generally, the seakeeping constraints on skimmers are even higher than on barriers. The reason for this is that the skimming elements of these devices must be kept in the oil most of the time for high efficiency. If the skimming elements spend much of the time in the air or in the water, poor oil collection efficiency will result. Studies of the seakeeping motion of pollution control devices and the design of equipment which minimize adverse motions are matters which can be handled before oil spills. However, in spite of our ability to analyze the seakeeping characteristics of a wide variety of equipment types, very little work in this regard has taken place. The only extensive work on the seakeeping abilities of pollution control barriers has been that of Milgram (1971) and Milgram and O'Dea (1974). This work provided a framework for studying the barrier seakeeping problem and contained some preliminary experiments. A few barriers have been designed and built in accordance with some of the findings of this work. However, most of the pollution control barriers in existence today have far less adequate seakeeping motions. The reason for this seems to be due to the fact that less adequate barriers can be built in a way that is less expensive and that leads to barriers that are easier to handle than those having good seakeeping motions. However, their oil containment and collection efficiency is substantially lower than that of the better devices. At this time, it would be worthwhile to do more theoretical and experimental research on barrier seakeeping in order to quantify the degree to which containment and collection efficiency is lost as the features which lead to good seakeeping motions, but which are expensive, are reduced. It is important to note that nearly all of the required experiments can be done without the presence of oil and hence the work can be carried out and the fruits of this work used to produce useful equipment without there having been any oil in the water. Thus, this is a task to do before an oil spill, not during or after. Of course, evaluation of performance during an oil spill is useful for comparing predicted performance with actual performance in order to determine what, if any, equipment modifications should be made.

Mass Transport by Reflected Waves. It was mentioned above that the seakeeping requirements on skimmers are often stricter than those on barriers. In addition, another seakeeping effect is important in the case of skimmers. When an external device interacts with waves, it reflects some of these waves. In a system with oil floating on water, there are two different types of waves of importance. The normal waves at sea are of one specific type. The second type is one which moves oil rapidly in the direction that the wave propagates. However, the reflected waves contain both types. As a result, a device which reflects many waves when floating in an oil spill tends to drive the oil away from itself. In the case of a skimmer under some sea conditions, this effect can lead to a device not being able to collect any oil at all! Thus, the interaction of the device with the oil through the phenomenon of reflected waves is especially important. This effect has not been studied in detail for many of the skimming devices presently in existence. It needs to be studied now in order to determine which devices are the most appropriate ones to use on oil spills and it needs to be studied during spill cleanup in order to obtain a confidence factor to place on the work that is to be done.

Modes of Hydrodynamic Failure of Oil Barriers. Oil barriers form a fundamental line of defense against damage from oil spills. They can be used in several ways. One is to protect vulnerable areas. Another is in skimming systems. Once oil has spread on the sea, it is so thin that the only device which can encounter the oil at a high rate is an oil boom. Therefore, massive spill cleanup at sea can only take place with towed oil booms having skimmers built into the booms or used within the U-shaped configuration formed by the towed boom. In the case of the *Argo Merchant* oil spill, the oil was No. 6 fuel oil and the temperature was very low. This combination resulted in the oil being extremely viscous (the author measured kinematic viscosities on the order of 70,000 centistokes). Hardly any pumping systems could handle so viscous an oil so it would not have been possible to actually collect the *Argo Merchant* oil from the surface of the sea unless we had special skimming devices for oil of this type. Since we do not have such devices, what could we have done had the oil threatened shore? It would have been possible to trap much of the oil in towed barriers and then to tow these barriers containing much of the oil far out to sea in hopes that the oil would be degraded or the weather direction would change before that oil returned to the shoreline. Thus we see another potentially very important use of barriers.

Early oil barriers generally suffered from inadequate strength and inadequate seakeeping ability. Now, some barriers are available which are strong enough to maintain structural integrity and which have sufficiently good seakeeping ability to follow the wave motion in moderate waves (typically in waves up to about 2 meters high, and higher waves when they are of limited steepness). Remaining problems with the use of barriers include two modes of hydrodynamic containment failure wherein oil goes beneath the barrier; one being called drainage failure and the other being called entrainment failure. Drainage failure is easier to understand and easier to deal with. Basically, when a barrier is towed faster and faster the thickness of the oil pool at the base of the U-shaped configuration gets larger and larger. Eventually, the oil becomes so deep that it passes beneath the barrier. This occurs before the depth of the pool equals the barrier draft because the pressure distribution associated with towing a barrier results in a "suction effect". It is always possible, in principle, to avoid drainage failure at any particular tow speed by using a sufficiently deep barrier.

Entrainment failure, on the other hand, cannot be prevented at arbitrary towing speeds because this mode of failure has nothing to do with the details of the barrier itself. It has to do with the fact that the interface between the floating oil pool and the water becomes unstable when the water speed relative to the oil is sufficiently large. Figure 6 is a sequence of sideview photographs of a restrained oil layer in an experimental flume at MIT for various current speeds ranging from 15 to 46 cm/sec. The figure shows that the oil-water interface is very smooth in a current of 15 cm/sec. At 23 cm/sec, a few waves on the interface are formed and a slightly bulbous region, called a headwave, is generated just behind the leading edge of the slick. These features are considerably more apparent at a current speed of 30 cm/sec and they are further amplified at a speed of 38 cm/sec. At a speed of 46 cm/sec the unsteady motion has become sufficiently

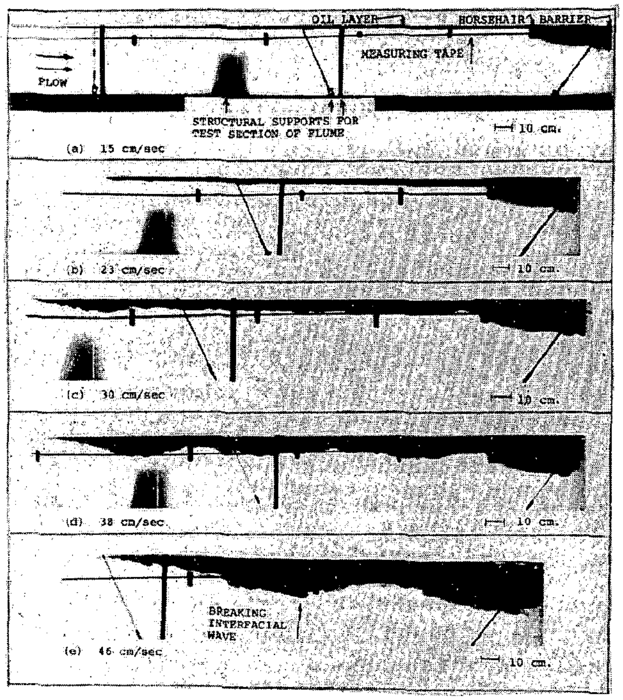


Figure 6. *Photographs of a Restrained Layer of Dyed Heavy Mineral Oil at Various Flow Speeds. On each photograph the flow speed and length scale are shown.*

violent for the interfacial waves to just begin to break and thereby generate droplets of oil which can become entrained in the flowing water. This happens to oil spills at sea, and when the droplets of oil in the water pass beneath the boom, we have containment failure due to entrainment.

Although the existence of the entrainment problem has been known for several years, it is only very recently that the fundamental fluid mechanics which cause it have begun to be understood. Milgram and Van Houten (1978) have conclusively confirmed the hypothesis of Leibovich (1976) that the short interfacial waves are Kelvin-Helmholtz waves and the oil droplets result from the breaking of these waves.

Although we have learned a great deal about the conditions under which the Kelvin-Helmholtz waves are generated, there is still much to learn about the conditions under which they break and form droplets. For example, in the experiments carried out by Milgram and Van Houten, it was found that droplet generation began with a diesel oil slick at half the relative current speed as it began with a slick of the Algerian crude oil called Arzew in spite of the fact that the two types of oil had almost identical densities, viscosities, interfacial tensions, and surface tensions. Since these measurements are basically "bulk measurements", it seems likely that the differences have something to do with the fact that the crude oil is a multi-component material. The details of droplet generation of multi-component materials need to be studied further. We know very little about the interfacial wave breaking and resulting entrainment from slicks of very viscous oils like that of the *Argo Merchant.* This information is of crucial importance to the on-scene coordinator if he is to arrange for spill containment and cleanup since the speed at which oil booms should be towed has a direct effect on equipment operations and on overall logistics.

When oil droplets are formed by entrainment, they slowly rise. Three possible things can happen to a droplet. First of all, it may initially be driven down so deep that it does not rise up to the slick before it has passed beneath the boom and is therefore lost by entrainment failure. Secondly, it may rise to the slick but not recoalesce before it moves to the boom where it is easily torn away from the slick and drawn beneath the boom. Thirdly, it may rise to the slick and recoalesce to the slick so that it is not lost by entrainment. Clearly, the third possibility occurs more frequently when there is a long oil slick contained in a barrier than when there is a short slick. No detailed observational or quantitative experiments have ever been made with long oil slicks in barriers. Two sets of experiments with quantitative measurements and careful underwater observations were made with relatively short pools of contained oil as reported by Tierney (1975). These experiments were made with between 28,000 and 40,000 gallons of oil in sections of the U.S. Coast Guard barrier that were 1,000 feet long. Such barriers can hold about 500,000 gallons of oil. Thus, with the booms holding less than 1/10th of their ultimate capacity, the slicks were quite short and the space available for droplet recoalescence was small.

Generally, it has been found that oil booms lose oil by entrainment failure at towing speeds in excess of one knot (52 cm/sec). An important question is: Can oil booms which are deep enough to prevent drainage failure be towed at substantially higher speeds than one knot and not suffer excessive entrainment failure if the oil slick is relatively long (say 150 meters or more)? That question can only really be answered by quantitative experiments and careful observation of oil booms containing enormous quantities of oil during actual large oil spill containment and cleanup operations. Such measurements and observations have never been made and should be carefully planned as part of our oil spill response measures.

Conclusions

In the above, I have attempted to show that there is an enormous amount of technical work remaining to be done in studying the physical phenomena related to oil spills. Some of the phenomena can be studied theoretically and in laboratories, some can be studied at sea without oil, some can be studied at sea with small quantities of oil, and some must be studied at sea with very large quantities of oil. All but the last two groups can be handled by normal well planned scientific efforts, if properly funded. Studies at sea with small quantities of oil are often hard to do because it is sometimes difficult to obtain permission to spill oil. Arrangements for the required tests need to be made in a reasonable way. Studies with very large quantities of oil can only be done during the occurrence of major oil spills. It is not possible to plan such studies once a spill has occurred. Extensive initial planning and preparedness is needed in order to obtain the maximum amount of information which can be learned from each spill. This requires a substantial financial commitment. However, without it we will never be in an improved position to answer the important questions that arise each time oil is spilled nor will we be able to reduce the cost and environmental damage of oil spills to the extent that is technologically feasible.

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Chronology of Events and Oil Slicks From the *Argo Merchant*

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Abstract

The operational and scientific events associated with the *Argo Merchant* oil spill are presented in the context of the condition of the vessel and the location of the spilled oil.

Chronology of Events

The purpose of this presentation is to give an overview of the *Argo Merchant* oil spill during the period of 15-31 December 1976. While not going into detail on the field and theoretical studies that accompanied and followed this spectacular event, this overview is intended to "set the stage" for the physical, chemical, and biological studies to be reported on during the remainder of this Symposium.

When the *Argo Merchant* went aground on the morning of 15 December 1976, no one was around to evaluate the extent of the initial spill. The first scientific observations of the scene were made by Elaine Chan of NOAA and Gary Hufford of the U.S. Coast Guard R&D Center. They flew to the scene in a chartered single-engine Cessna 182, on Thursday morning, 16 December 1976. [Slide 1; Photograph 1, p. III-3, Grose and Mattson, 1977]*. Chan and Hufford reported an oil slick extending approximately two miles from north to south and four miles east to west, being fed by a streamer of oil bearing about 240° from the vessel. That afternoon, Peter Grose, Craig Hooper, and I flew to the scene of the grounding in the same plane, only to find that fog had obscured visibility so much that we could not approach the vessel. What we did see, to the west of the *Argo Merchant,* was a nearly continuous oil slick extending several miles from north to south.

The biggest break of the *Argo Merchant* spill came that night when that same fog forced Joe Deaver, of the Coast Guard's Oceanographic Unit, to land at Otis AFB on Cape Cod. Deaver's twin-engined HU-16 was far superior to the rented Cessna for operations at sea, and Deaver was carrying an infrared radiometer for use in thermal mapping of the Gulf Stream. The Coast Guard agreed with the few scientists present that night at Otis AFB to send Deaver out the next morning to map the extent of the oil slick emanating from the grounded tanker.

The next morning, Friday, 17 December 1977, Peter Grose and Gary Hufford accompanied Deaver in the first mapping effort. Visiting the grounding scene first [Slide 2; Photograph 2, p. III-3, Grose and Mattson, 1977], they reported a heavy concentration of oil extending 5 miles to the northwest, towards Nantucket, then curving 3½ miles to the west [Slide 3, Figure 1]. They reported that the oil looked like "an asphalt road," with no thin sheen surrounding it. This is not unusual, looking back over the event, as the weather that day was relatively poor, with 17 knot winds, rain and snow, and the seas were showing 2 to 4 ft. waves and swells. All through the *Argo Merchant* experience, much of the oil slick would "disappear" on rough days, only to reappear almost undiminished when the weather would clear. A power failure aboard Deaver's plane terminated Friday's

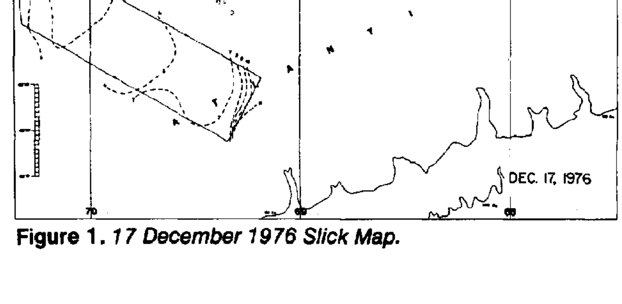

Figure 1. *17 December 1976 Slick Map.*

*Copies of the color slides may be found in Appendix III of Grose and Mattson, 1977.

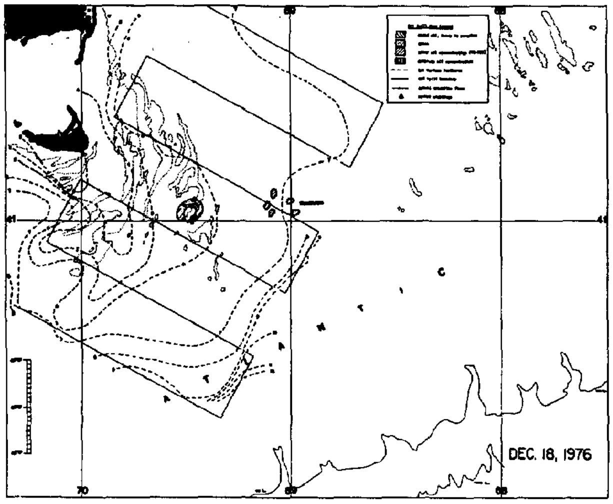

Figure 2. *18 December 1976 Slick Map.*

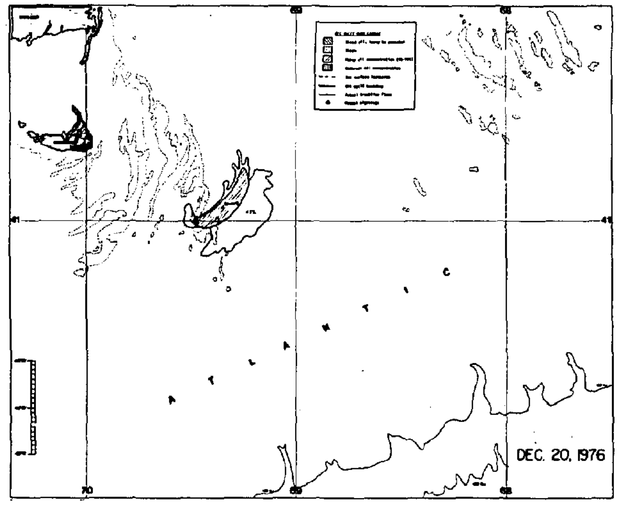

Figure 4. *20 December 1976 Slick Map.*

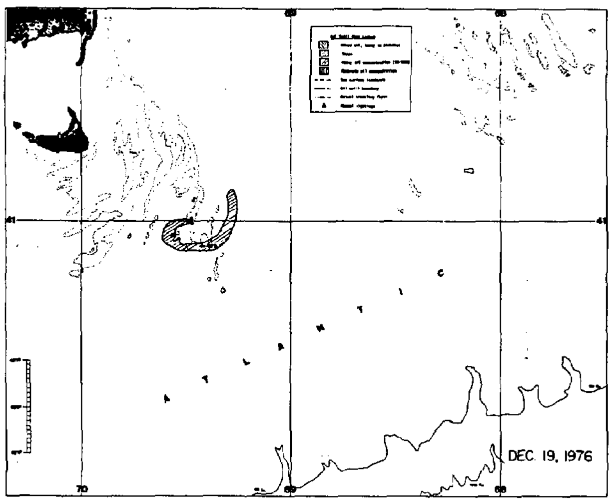

Figure 3. *19 December 1976 Slick Map.*

search pattern prematurely, and only the limited rectangular flight path shown on Figure 1 was carried out. One of Deaver's primary objectives during his initial overflights, one of many that lost out to the broader objective of "mapping", was to use his infrared radiometer to measure oil slick temperatures, particularly to see whether the thin and thick regions of oil differed either positively or negatively from the surface water temperature. The temperature isopleths on the slick maps for December 17, 18, 21, 23, and 24 represent that effort. By the 31st, and January 2nd and 3rd, the rationale for thermal mapping had changed to one of locating the edge of the Gulf Stream, as well as a suspected "ring" on the western edge of the Stream.

By Saturday, 18 December, the counter-clockwise shape of the slick, due to rotary tidal currents, was distinctly visible [Slide 4, Figure 2], and on Sunday, a beautifully calm day, the slick had grown into a 16-mile long "horseshoe", as shown in Figure 3 [Slide 5], and in the photograph taken from a Coast Guard helicopter from the east of the grounded tanker [Slide 6; Photograph 4, p. III-3, Grose and Mattson, 1977]. The shape of the slick on 19 December is best exemplified by the composite photomosaic prepared by NASA from their overflights of that day [Slide 7; p. III-12, Grose and Mattson, 1977].

By Sunday, the 19th, we had become aware that the "asphalt highway" seen from the HU-16 overflight was in reality a mixture of thick "pancakes" surrounded by thin "sheen". The thickness of one such pancake was estimated to be on the order of one centimeter. From the helicopter, Jerry Galt and I estimated the "pancake" coverage to be no more than 1/10 of the total observable slick, but even this estimate produced a slick "volume" that exceeded the *Argo Merchant's* entire cargo by about a factor of three. Meanwhile, the figure arrived at by Deaver from his HU-16 observations was something between 90 and 100% "thick" oil on the 19th. Rather than try to change the aerial estimation of "pancake" coverage, Deaver had a "look-see" constructed of Plexiglas with a 50-square grid etched on it, so that he could give consistent estimates from day-to-day. We hoped that his estimates could eventually be "ground-truthed" with some of the many aerial photographs that were being taken by NASA and by BLM's contractor, Aero-Marine Surveys, Inc.

On Monday, the 20th, the weather was reasonably good, and Deaver, Dave Kennedy, Captain Lynn Hein, the on-scene coordinator, and I set out in an H-3 helicopter to map the slick, and to conduct some differential oil-water velocity measurements. The horseshoe shape of the previous day had given way to the banana-shaped slick shown in Figure 4 [Slide 8], and when this information was telephoned to Jerry Galt at WHOI, just before *Oceanus* departed on her first cruise during the incident, it appeared that the oil had broken out of the tidally-influenced regime and was headed to the northeast. On *Oceanus*, this was the interpretation given to the observations, and the cruise was planned to the northeast of the oil slick, as shown, on 20 December.

On Tuesday, 21 December 1976, all hell broke loose. The *Argo Merchant* broke in two aft of the king post at 0835 [Slide 9; Photograph 7, p. III-4, Grose and Mattson, 1977], releasing 1.5 million gallons of oil "all over the place," according to Deaver and Dave Kennedy, who were in the HU-16. The slick map prepared by Deaver that day included much of the oil released in the first breakup, and is shown

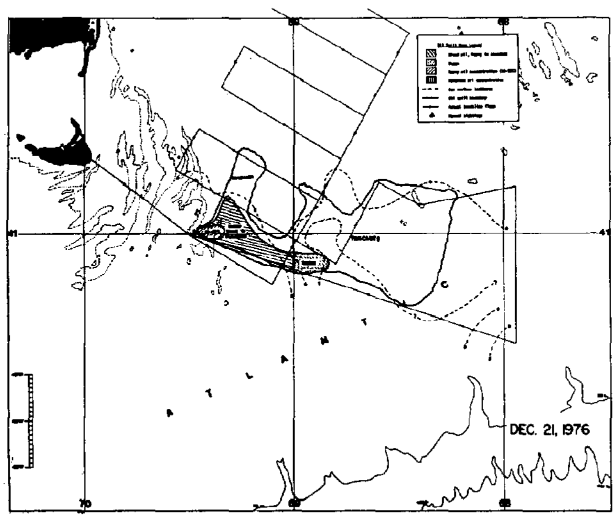

Figure 5. *21 December 1976 Slick Map.*

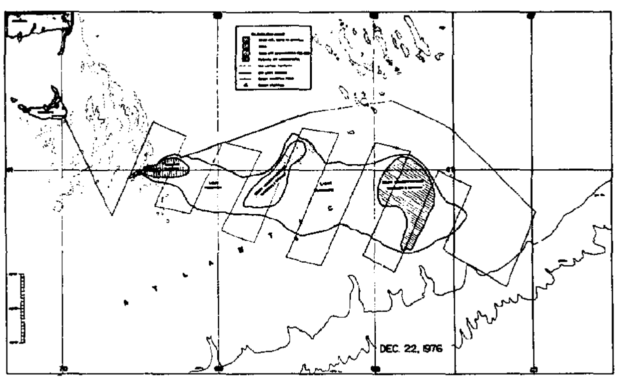

Figure 6. *22 December 1976 Slick Map.*

in *Figure* 5 [Slide 10]. By then, there literally *was* oil "all over the place".

On Wednesday the 22nd, while many of our colleagues, who were to eventually show an interest in the spill, were attending an EPA-called meeting at the Federal Building in Boston, the *Argo Merchant* split again at 0730, releasing another 1.5 million gallons (the amount estimated to be contained in three tanks across the vessel) into a heavy sea (winds up to 50 knots, seas to fifteen feet). While Deaver and Kennedy carried out a six-hour long mapping flight, with the result shown in Figure 6 [Slide 11], Elaine Chan and Scott Fortier (USCG R&D Center) went out to the scene in a helicopter to take samples of the thick oil that was surrounding the wreckage at that time. In a part of the *Argo Merchant* story not well-circulated to date, the HU-16 carrying Deaver and Kennedy lost an engine on this mapping flight, and the engine caught fire on landing at Otis AFB.

On Thursday, 23 December, a number of valuable pieces in the puzzle were collected. First, Dave Kennedy took a team of four U.S. Navy divers out to the scene in order to photograph the underside of the floating "pancakes", looking for streamers, "skegs", or anything else that might be peculiar to that situation, and to photograph the sandy bottom in the vicinity of the wreck to determine whether any of the oil had sunk in noticeable quantities in the seven days since the grounding. They returned before noon with 15 minutes of movie film, a roll

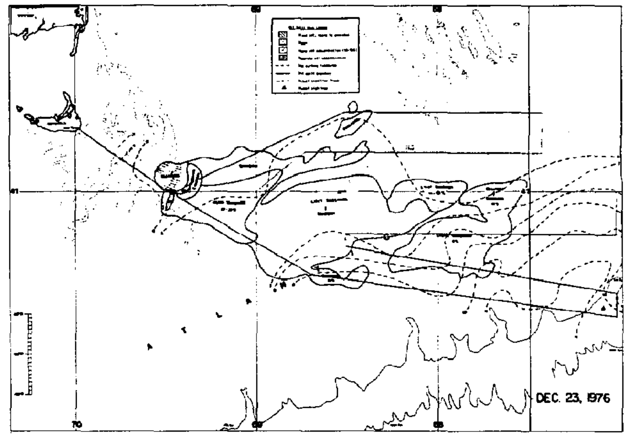

Figure 7. *23 December 1976 Slick Map.*

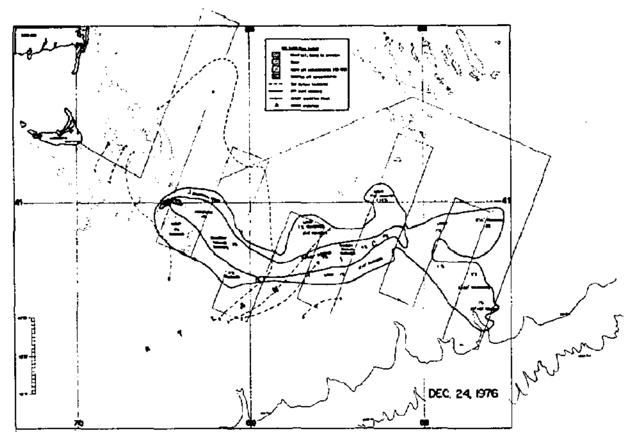

Figure 8. *24 December 1976 Slick Map.*

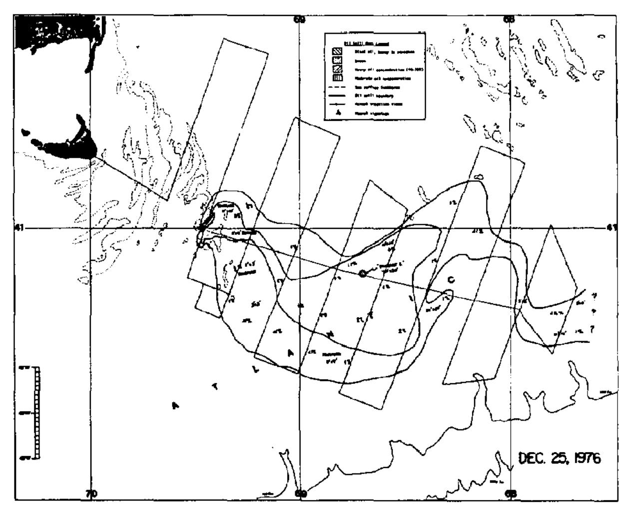

Figure 9. *25 December 1976 Slick Map.*

of underwater slides showing the underside of the slick, and their own descriptions of what they had seen. In addition, Deaver conducted another 6-hour mapping survey, with the results shown in Figure 7 [Slide 13].

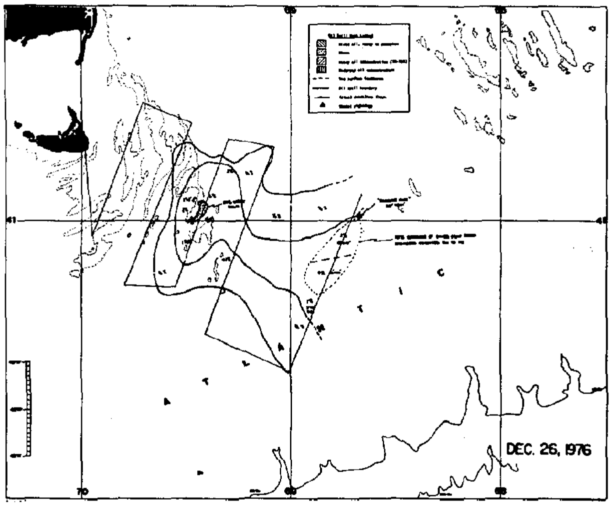

Figure 10. *26 December 1976 Slick Map.*

On the 24th and 25th, Joe Deaver and Al Kegler (of the Alaska Dept. of Fish and Game) continued the mapping, as shown in Figures 8 and 9 [Slides 14, 15], although by Christmas Day, the mapping took just under seven hours in the HU-16, and it had become impossible to map the easterly extent of the slick in that time. Christmas Day did produce a bonus, however, as Deaver and Kegler located a huge (300' x 700', probably over ½ million gallons) pancake, shown in Figure 9 [Slide 16; Photograph 38, p. III-21, Grose and Mattson, 1977]. Because of its size, we guessed that "Pancake I" comprised the entire cargo of one of the tanks that split open on December 21 or 22.

At that point, by Sunday December 26, mapping of the extent of the slick, because of its huge size, had to be reduced in priority as other objectives became important. The first of these originated from a weather forecast on Christmas Day that called for sustained easterly winds that night. Computer projections being carried out by the Coast Guard based on Deaver's maps predicted a near-landfall of the eastern edge of the slick on Nantucket Island sometime Sunday. Therefore, when Deaver, Kegler, and Ed Myers (of NOAA) took off in sleet and snow at 0915 on the 26th, they deployed some 4,000 drift cards at locations between the last reported easterly edge of the slick and Nantucket Island. Fortunately, the easterly winds were short-lived and the oil never came ashore. Neither, for that matter, did a single one of 9,000 drift cards deployed on December 26 and 27. After dropping their drift cards on December 26th, Deaver and his crew proceeded to relocate "Pancake I", shown on Figure 10 [Slide 17].

On the 27th of December (Monday), the final "complete" map of the slick was made, though the easternmost boundary could not be ascertained as shown in Figure 11 [Slide 18]. In addition, the Coast Guard conducted a "burn test" that day [Slide 19; Photograph 43, p. III-22, Grose and Mattson, 1977] on one of the huge floating pancakes (this one was estimated to be about 300 ft. in diameter). Needless to say, the pancake did not burn.

Poor weather precluded any aerial observations in the next two days, December 28th and 29th. On the 30th, the Coast Guard HU-16 lost an engine and caught fire on takeoff, terminating that day's operations. On the 31st of December, Deaver made a flight to the edge of the Gulf Stream in an effort to determine whether the slick had entered the Stream. That evening, in a five-hour helicopter flight to the eastern portion of the slick, Peter Grose and Marilyn Pizzello (NOAA) dropped a satellite-trackable buoy into the middle of what they thought was "Pancake I".

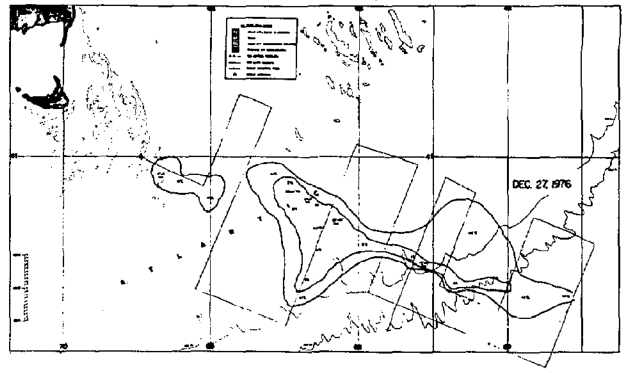

Figure 11. *27 December 1976 Slick Map.*

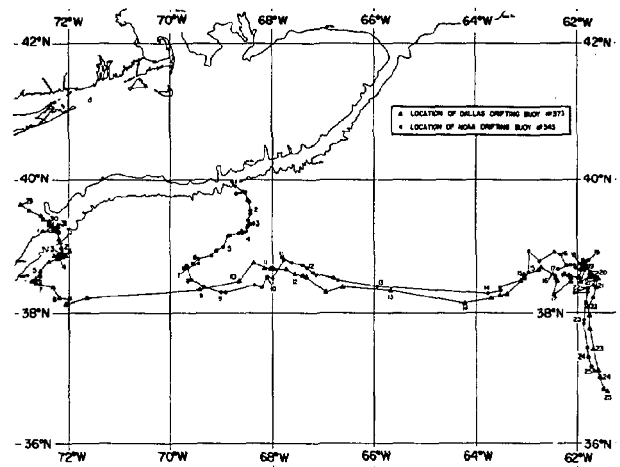

Figure 12. *Track Lines of Drifting Buoys.*

Relying on the buoy, rather than straining people and aircraft to their limits, marked the beginning of the New Year. The slick, if it could still be called that, covered thousands of square miles of sea surface, and was simply unmappable. The buoy positions for the next 25 days are shown in Figure 12 [Slide 20]. This buoy stopped transmitting in September 1977; at that time, the buoy was reported to be about 200 miles off the Azore Islands. Thus was marked an end to this, one of the most spectacular, and probably the most closely-watched, oil spills of all time.

The Behavior of Floating Oil From the *Argo Merchant*

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Abstract

The *Argo Merchant* oil formed thick pancakes surrounded by a thin sheen most likely because of fractionation of the bulk oil and spreading of the lighter components controlled by lower surface tensions. Measured differential velocities of the pancakes and surface waters are consistent with a wave/oil interaction model that predicts oil velocities of twice the surface Stokes drift. The thicknesses of the oil pancakes are not consistent with a model that considers only static forces. However, when the dynamics of the oil movement are included in the model, the predicted results are more realistic, with thicknesses related to the square root of the surface tension at low speeds and to the square of the oil/water differential velocity at higher speeds.

Discussion

During the *Argo Merchant* oil spill, unique opportunities arose for observing the physical behavior of the floating No. 6 oil. This paper describes some of the observations made during the oil spill (Grose and Mattson, 1977). In particular, the appearance of the pancakes that the oil formed, their morphology, and their movement are discussed. These observations are examined in light of models that attempt to explain them.

As the oil flowed out of the tanker, it was advected away by primarily tidal currents. Although in gross appearance the oil slick appeared to be continuous (Slide 4*), in reality it was composed of thick oil pancakes surrounded by a thin sheen and open water. The proportions of these three components of a typical oiled area shortly after the spill were estimated roughly as 40% clear water, 60% sheen, and less than 1% of the area covered by the thick pancakes (Slide 39). The pancakes could be differentiated from the sheen by their smooth black surfaces, while the sheen was irridescent and easily broken by waves. The cause of the sheen formation is most likely chemical fractionation (Phillips and Groseva, 1975), where the lighter fractions physically separated from the bulk of the oil in the pancake and spread into a thin lens because of lower surface tensions. The pancakes were fluid and changed shapes rapidly. These shape changes appear to be related to the differential velocity of the oil relative to the surface waters, rather than to the spreading of the oil into a thinner lens. This conclusion is drawn from the observation that the pancakes did not diminish in thickness with time.

On December 23, 1976, divers from the U.S. Navy Audio Visual Command dived beneath the oil slick and photographed the bottom and edges of an oil pancake (Slide 30). Three important conclusions can be drawn from the photographs and the observations by the divers. First, the bottom of the pancake they saw was similar in appearance to its top surface; that is, it was relatively flat and smooth and, most important, did not have a keel or other protuberances extending into the water below. Second, the edges of the pancake were well defined and relatively square in shape. They did not appear to taper in thickness as might be expected with a lens shape. Also, the interface between the oil and water was well defined and there was no visible boundary layer between them other than the interface itself. In other words, while the pancake was not well coupled to the water column, neither was it totally decoupled by streamlining. Third, when the pancake was broken by the divers' air bubbles, the rend would heal within a matter of seconds, indicating that there were forces acting on or within the pancake to maintain it as a distinct entity.

It has been known for some time that oil moves faster than surface waters. Several experiments were conducted to determine this relative velocity during the *Argo Merchant* spill. The best documented experiment was conducted at 1100 on December 19, 1976, at the end of a 1000-foot streamer of oil heading east near the far end of the slick (Slide 22, right hand corner near 41 03'N; 69 19'W). A line of dye pills was dropped from a helicopter onto the water directly downwind of the oil and the oil overtaking the dye was observed (Slide 35). The dye pills were dropped approximately 90 ft. apart. After 205

*Copies of the color slides may be found in Appendix III of Grose and Mattson, 1977.

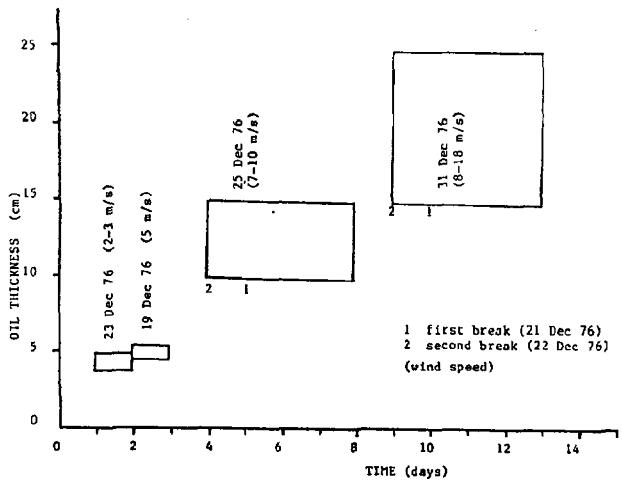

Figure 1. *Estimated Oil Thickness As a Function of Estimated Age.*

sec (Slide 36) the oil had reached the nearest dye pill. The velocity of the oil relative to the surface water (5 cm) was calculated to be 5.6 cm/s in an easterly (downwind) direction. With these two slides one can also measure the elongation of the dye tails that resulted from a shear between the surface and about 50 cm depth as well as from some windage on the pills themselves. The measured elongation velocity was 5.6 cm/s, again in the downwind direction. Relative to wind speed, both of these speeds are about 1.1% of those measured at 19 m elevation by a Coast Guard cutter 7 miles away. The differential velocity measurements agree quite nicely with the model of oil movement proposed by Milgram (1977A, B). In this model the oil surface is predicted to move at about twice the Stokes drift speed as an upper limit because of interaction with waves generated by local winds. The elongation velocity of the dye tails should be a good approximation of the Stokes drift.

On several occasions visual estimates of the thickness of the oil pancakes were made. Figure 1 illustrates four such estimates as a function of the age of the pancake. The thickness appears to increase with age, but there were differences in wind speeds, and the thinner estimates were made under lighter wind conditions. The increase in thickness is of considerable interest because thick oil is easier to recover and because this phenomenon appears to be fundamental to the dynamics of some spilled oils. One possible explanation for the variation is an increase in surface tension as the oil ages. Langmuir (1933) developed a relationship between the surface tensions and densities of a two-part immiscible fluid system with the thickness of the fluid lens. In his model the thickness is a function of the square root of the spreading force (FS) times the buoyancy term (A) derived from the densities. Applying actual measurements of the *Argo Merchant* oil gives a computed thickness for the pancakes of 1 cm. Using an estimated maximum surface tension (double) to which the oil might have aged results in a maximum computed thickness of only 2 cm. This computation does not agree with the observations in spite of being based on unreasonably large surface tensions. However, the observations were not made under the static conditions that apply to Langmuir's model. The oil was moving faster than the surface water and thus one would expect a compressive force to be acting on the oil caused by a drag exerted on a pancake as it moves through the surface waters and by the force accelerating it. This compressive force would act to increase the thickness of the pancakes. For this model we have a balance between the integrated hydrostatic forces and the surface tensions of the two oil surfaces within the pancake, and the equivalent integrated hydrostatic pressure, water surface tension, and the drag force outside the oil. This model, which is identical to Langmuir's model with the addition of the drag force, is represented numerically by

$$0.5 * \rho_O * g * T^2 \cdot \gamma_O \cdot \gamma_{OW} = 0.5 \cdot \rho_W \cdot g \cdot (T \cdot \rho_O/\rho_W)^2 \cdot \gamma_W + FD \quad (1)$$

where the subscript O refers to the oil and W to the water, γ are surface tensions, ρ are densities, g is gravitational acceleration. T is the thickness of the oil lens, and FD is the drag force. From dimensional reasoning, this drag force should be proportional to the thickness, the square of the oil velocity (U), and a drag coefficient (CD), which is in turn a function of the Reynolds number for the water:

$$FD = CD * T * U^2 \quad (2)$$

Substituting (2) into the quadratic (1) and solving for the thickness:

$$T = CD * U^2 / A + (U^4 - 2 * A * FS)^{1/2} / A \quad (3)$$

In eq. (3) we have defined the spreading force FS and a density function A to simplify computations:

$$FS = \gamma_W \cdot \gamma_O \cdot \gamma_{OW} \quad (4)$$

and

$$A = g * (\rho_W \cdot \rho_O) * \rho_O / \rho_W \quad (5)$$

If we assume that the drag coefficient for the oil lens is approximated by the coefficient for an infinite cylinder, at Reynolds numbers of approximately 2000 for the observed thickness and speed we have:

$$CD = 1. \quad (6)$$

An estimate of the spreading force (FS) can be made by using measured values for the surface tensions of the oil and the water of 35 and 72 dynes/cm, and assuming the water/oil interface tension is 69 dynes/cm. This assumed value is based on Milgram's measurements of the surface tension of water with a thin film of oil on top of 59 and of water pipetted from directly beneath oil of 79 dynes/cm (Grose and Mattson, 1977, pg. 71). These measurements and assumed values result in a spreading force of -32 dynes/cm. A numerical value of A, eq. (5), is computed to be 62 from measured specific gravities of the oil and water of 0.96 and 1.028 respectively. Furthermore, we can approximate the speed of the pancake as 1.1% of the wind speed from the experiments described earlier. Substituting the above values into eq. (3) thicknesses of 1.5,

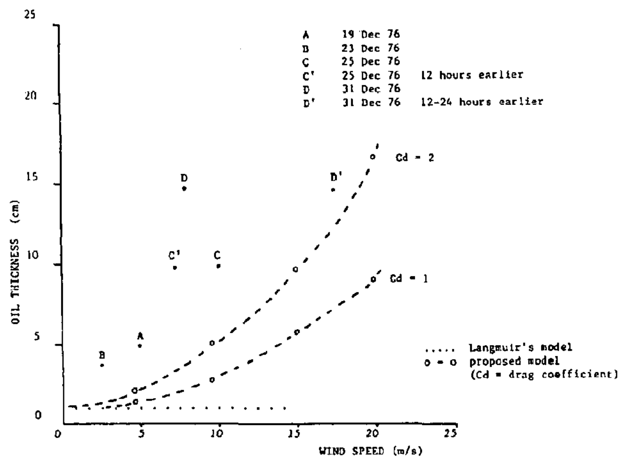

Figure 2. *Oil Thickness As a Function of Wind Speed.*

3.0, 5.4, and 8.8 cm are computed for wind speeds of 5, 10, 15, and 20 m/s (Figure 2). Doubling the drag coefficient (CD) to 2 yields an even better agreement as indicated in this figure. While these thickness values are not as large as the visual estimates indicated in the figure, they do bring the theory closer to the observations and indicate that the hydrodynamics of the oil pancakes is important in determining their behavior. What remains is to properly measure the drag coefficient for an oil pancake, but this is beyond the scope of our discussion here.

As the oil on the water surface ages, it will weather by fractionation and evaporation. Because of the weathering, one would expect the viscosity to increase. This viscosity increase does not cause the pancake to become thicker other than by slightly increasing its relative velocity, as indicated by Milgram's model, but viscosity does effectively increase the amount of time required for the pancake to reach equilibrium with the forces acting on it. Therefore, some form of time integration of the forces acting on the pancake must be used when relating Eq. (3) to the real world, which is in dynamic rather than static equilibrium. This may help to explain the deviant point in Figure 2 for December 31. While the winds averaged only 7.5 m/s for the 4 hours before this measurement, from 24 to 12 hours before the measurement they averaged 18 m/s. That the viscosity of the oil was high is not the question, since a piece of 2 x 4 lumber on the pancake surface was observed to be sitting with its long face vertical.

Without postulating increases in surface tensions, we thus find the data on pancake thickness increase to be consistent with almost all the facets of a model that moves oil by wind waves. The only prediction not supported by observations is the change in pancake speed between the top and bottom of the lens as observed by Milgram (1977B). Drift cards placed on pancakes did not tend to move toward the leading edge as is implied by a shear profile throughout the thickness of the pancake. While a shear must exist, it may be that it is concentrated at the oil/water interface. Certainly this needs to be investigated further, as the shear will directly influence the amount of oil that gets accommodated into the water column.

This paper has attempted to demonstrate that it is not sufficient to consider oil as a static substance on the water surface. The local dynamics appear to be critical in trying to predict its behavior. Some aspects of the postulated dynamics agree with the observations: Sheen formation controlled by fractionation and spreading dependent on surface tensions; differential velocities related to interaction of wind waves with oil pancakes; and to a limited extent oil thickness determined by surface tensions at low pancake speeds but by drag forces at higher speeds. However there are still some inconsistencies and many unknowns. Future research should be directed toward resolving these inconsistencies and unknowns. Among these are: Where is the shear located between the oil surface and the water below? What is the drag coefficient for an oil pancake? What are the streamlines for the water flow in the vicinity of a pancake? Once these questions have been answered, the models will be capable of predicting how the oil will behave in a more realistic manner.

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Can Oil Spill Movement Be Predicted?

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Abstract

On 15 December 1976 the *Argo Merchant* grounded on Nantucket Shoals approximately 28 miles southeast of Nantucket Island. Immediate forecasts of the movement of the oil should a spill occur from the ship were required by Coast Guard Marine Safety Office (MSO), Boston. A description of the forecasts provided to MSO, Boston, is provided. The method used for predicting the oil movement was a simple vector addition of the tidal velocity and 3.5% of the wind speed on an hourly basis. The lateral spread of oil was determined from the tidal velocities. Results of the forecasts compared to the actual movement of the oil are given, as well as a retrospective discussion of the validity of the techniques that were used.

Introduction

On 15 December 1976 the *Argo Merchant* grounded on Nantucket Shoals approximately 28 miles southeast of Nantucket Island (Figure 1). The Coast Guard R&D Center has been involved in developing forecasting techniques for predicting the movement of oil spills in estuarine and offshore areas. These techniques involve vector addition of the forces that move the oil. For estuarine areas this generally includes addition of wind, tide, and fresh water flow vectors; and wind, tide, and semi-permanent current vectors for offshore areas as shown by Hufford et al. (1975) and Lissauer and Bacon (1975). These techniques were applied to forecast the movement of oil from the *Argo Merchant.* Results of the forecast are given, as well as a retrospective discussion of the validity of the techniques used based on the actual movement of the spill.

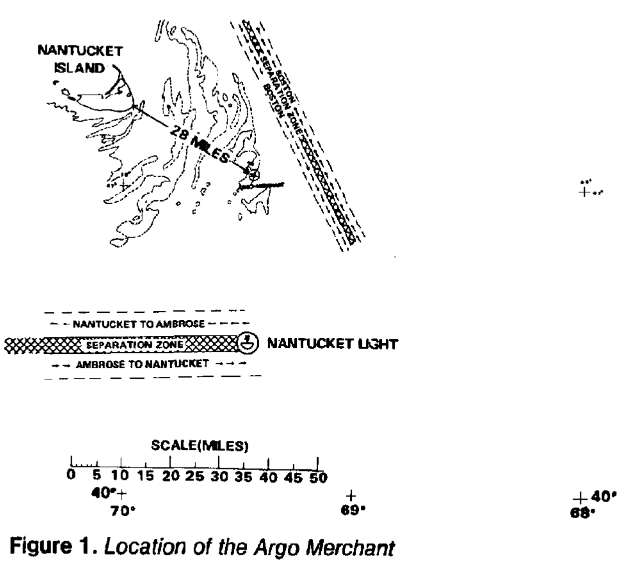

Figure 1. *Location of the Argo Merchant*

Forecast

Forecast of the movement of the oil began on 15 December 1977. Data for the forces which transport the oil were obtained and examined. The magnitude of the wind vector from predicted values of wind speed would move the oil at a rate of 0.5 to 1.5 knots in a downwind direction; the magnitude of the tidal currents would move the oil at 0.5 to 1.3 knots; the magnitude of the permanent currents in the area are approximately 0.1 to 0.2 knots. After comparing the magnitude of the forces that move the oil, it was determined that for short-term predictions (i.e., <12 hours) the tides and winds would control the movement of the oil. For long-term predictions the winds alone would dominate the movement of the oil. The method used for predicting the movement of the oil was a simple vector addition of the tidal vector and 3.5 percent of the wind speed on an hourly basis. The lateral movement of the oil was determined to be the magnitude of the tidal movement. This combined with the hourly vectorial movement of the oil showed the extreme estimate of the areal extent of the oil.

On 16 December at 0930, the U.S. Coast Guard Marine Safety Office (MSO), Boston, requested a forecast of the movement of oil should the tanker rupture. At 1135, MSO, Boston, was informed that the oil would move southeast for the next 24 to 48 hours. In addition, the oil would continue to move southeast to east through the weekend of 18 and 19 December. This forecast was based on the tides and the predicted winds supplied by the National Weather Service (NWS). MSO, Boston, was also informed that the oil would continue to move offshore as long as the winds were offshore.

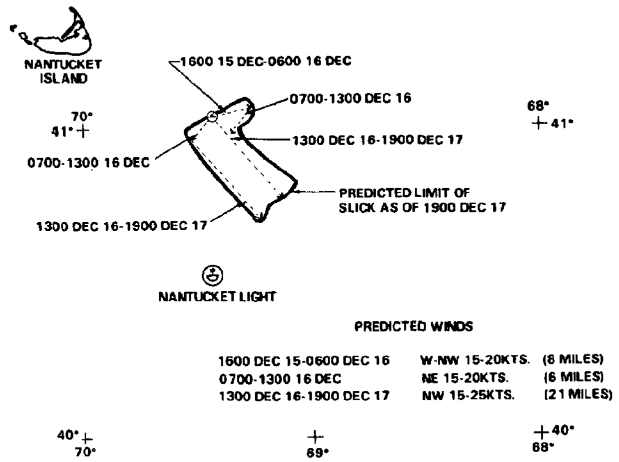

Figure 2. *Predicted Limit of Slick as of 1900 17 Dec.*

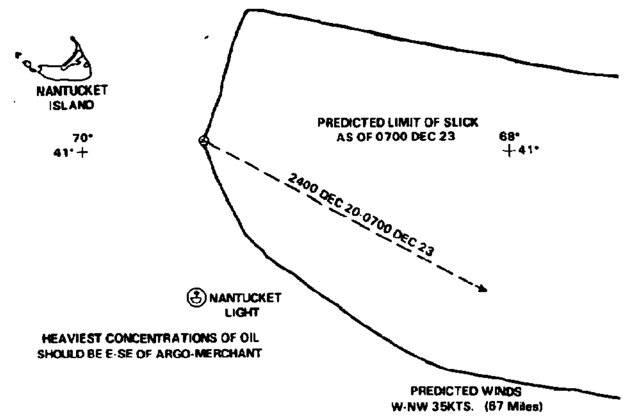

Figure 5. *Predicted Limit of Slick as of 0700 23 Dec.*

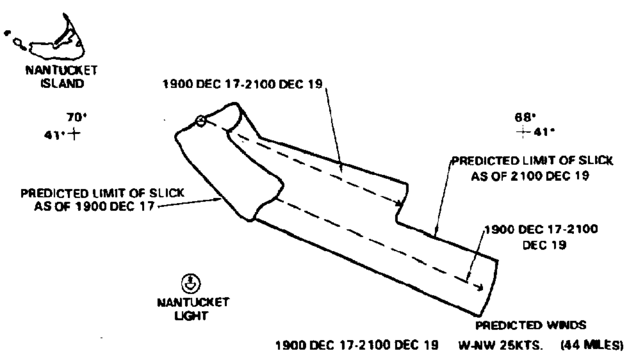

Figure 3. *Predicted Limit of Slick as of 2100 19 Dec.*

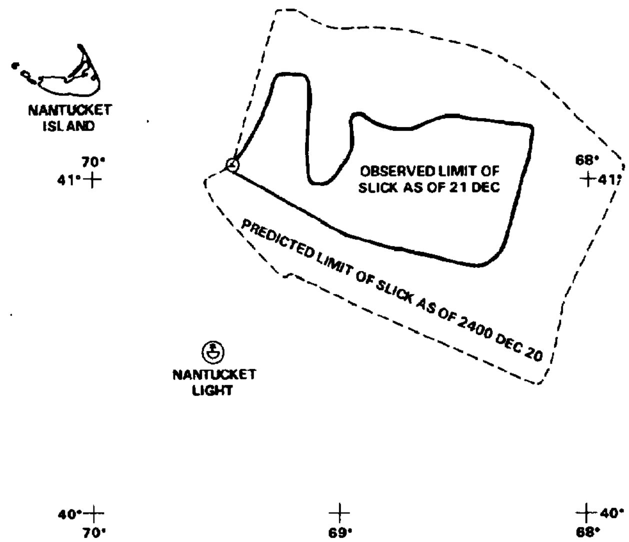

Figure 6. *Comparison of Observed and Predicted Limit of Slick as of 21 Dec.*

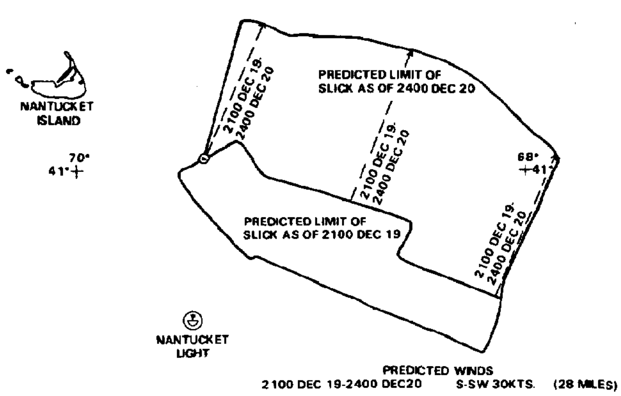

Figure 4. *Predicted Limit of Slick as of 2400 20 Dec.*

Figures 2 through 5 depict the predicted movement of oil. These figures were the basis for the information which was transmitted to MSO, Boston. The long-term movement is based on the predicted winds as supplied by the NWS. Figure 2 shows the predicted limit of the slick as of 1900, 17 December. The predicted winds used for the forecast as well as the total movement of the oil caused by the predicted winds are shown. From 1600, 15 December to 0600, 16 December, the west-northwest winds and tides moved the oil eight miles to the east-northeast. From 0700 to 1300, 16 December, the northeast winds moved the oil towards the southwest a distance of six miles. The spill was treated as a continuous leak. Therefore, the oil movement was continuously predicted from the site of the *Argo Merchant.* This is the reason there are two vectors labeled 0700-1300 16 December. One of these vectors shows the transport of the oil that moved northeast prior to these wind conditions. The other vector shows the movement of oil from the wreck site during the period 0700-1300, 16 December. This process was used for the entire period. Thus the boundaries of the oil spill shown on Figures 2 through 5 are, in essence, an estimate of the extreme outer limits of the oil slick.

Figure 6 is a comparison of the observed limit of the slick on 21 December (obtained from overflights) and the

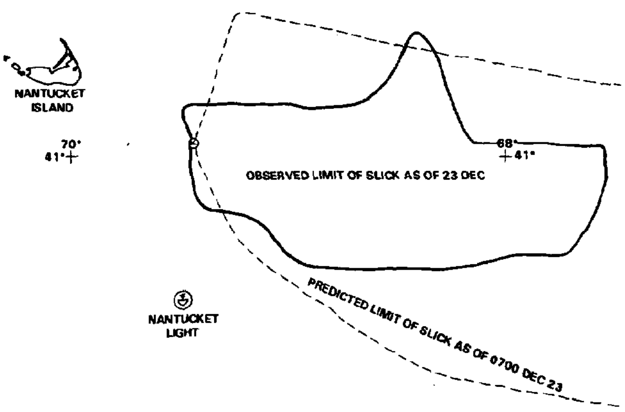

Figure 7. *Comparison of Observed and Predicted Limit of Slick as of 23 Dec.*

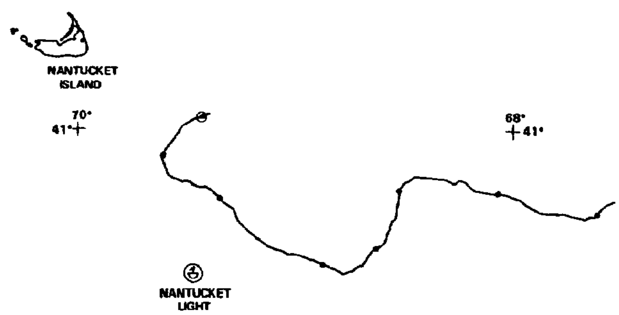

Figure 8. *Progressive Hourly Wind Vector Diagram Using 3.5% of the Wind Speed*

estimate of the slick limit predicted from the winds as of 2400, 20 December. Figure 7 is a comparison of the observed limit of the slick on 23 December and an estimate of the slick limit as of 0700, 23 December. Again, the observed limit of the slick was obtained from overflights of the area. In Figures 6 and 7 the predicted direction of movement of the oil is in excellent agreement with the observed movement. The predicted areal coverage for both figures is about twice the observed coverage. This entire prediction was accomplished in approximately three hours from the time of request. It indicates that vectorial addition of the forces that move the oil is an excellent method to obtain quick response answers to where the oil will go and when it will get there. Had the winds been onshore instead of offshore this method would have enabled cleanup equipment to be placed at strategic areas before the oil came ashore. In addition, it seems likely that had actual on-scene winds been used in the forecast rather than long-term predictions from NWS, the predicted movement and dispersion would have been even more precise.

Observations

Figure 8 is a progressive hourly wind vector diagram using 3.5 percent of the wind speed for the period 1600, 15 December to 0700, 23 December. The diagram was prepared from on-scene wind data collected by the

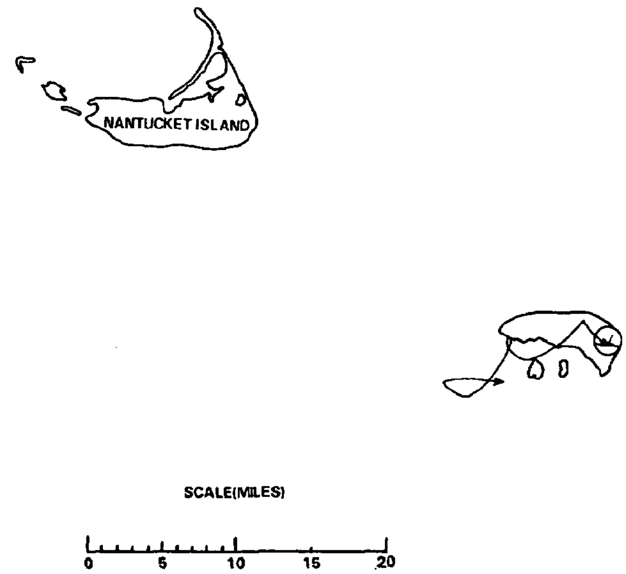

Figure 9. *Comparison of Observed Slick and Predicted Movement Caused by Tides and Wind*

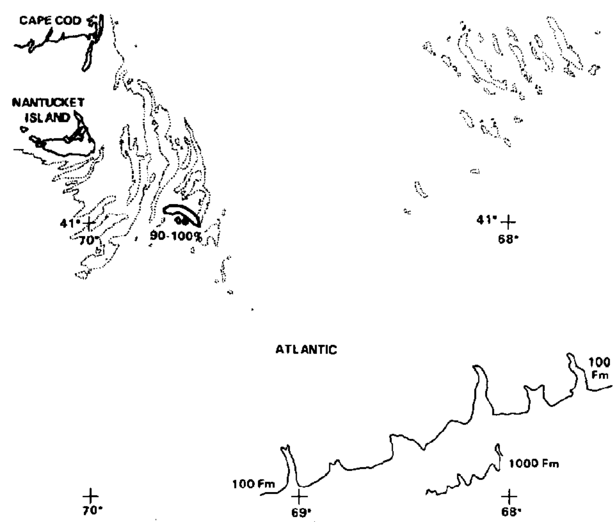

Figure 10. *Observed Area of Oil Spill on 17 Dec.*

USCGC *Vigilant.* This wind data and tidal data (from the charts) can be used to compare actual short-term movement of the oil with the predictive technique of adding winds and tides vectorially. In addition, the validity of using 3.5 percent of the wind speed in a downwind direction can be examined.

For short-term drift, Figure 9 gives a comparison of observed slick and predicted movement caused by tides and winds. The vector shows the predicted movement of the oil for the period 2400, 15 December 1976 to 0900, 17 December 1976. The outline of the slick was taken from Figure 10 which shows the observed slick determined near noon on 17 December. There is excellent agreement between the actual directional movement of

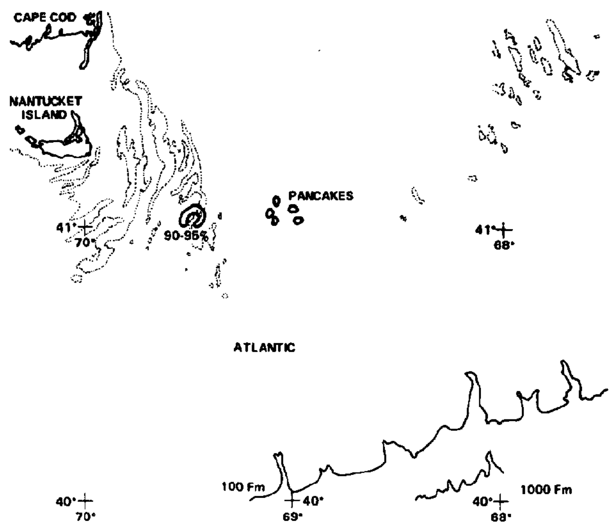

Figure 11. *Observed Area of Oil Spill on 18 Dec.*

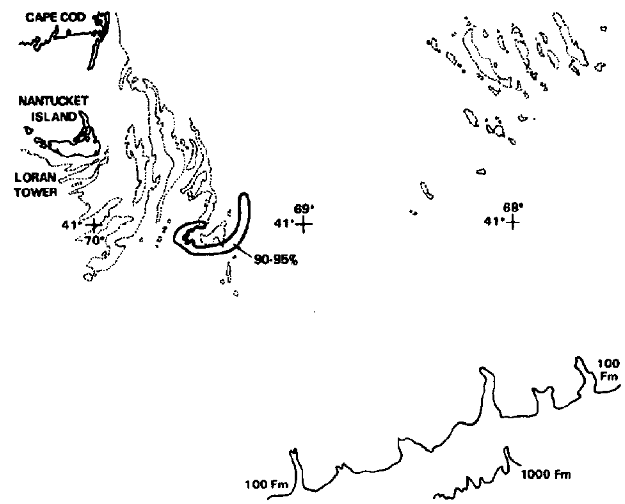

Figure 12. *Observed Area of Oil Spill on 19 Dec.*

the oil and the predicted movement as determined from tides and wind. In fact, it appears that 3.5 percent of the wind speed adequately describes this transport vector. The greatest error occurs in predicting the tidal component for each hour of movement.

During the period 15 December to 19 December, the total extent of the spill was not clearly defined in overflights. However, several observations of the movement of the oil during and after this period verify the techniques used. These observations are shown in Table 1.

The observed movement of the oil spill is documented in Figures 11 through 16. Table 1 indicates that the oil was moving westward bearing 240°T on 16 December. The wind vector during the morning of the 16th was 245°T. On 18 December, pancakes were found 27 miles east of the ship (090°T). The maximum eastward movement of the oil caused by the wind (Figure 8) is 31 miles bearing 130°T. Assuming this is the maximum eastward extent of the oil the computed wind factor for moving it would be 3.05 percent. Commencing on the

Table 1. Observations of Oil Movement

Date	*Actual Observations of Oil Movement*	*Predicted Movement of Oil Using 3.50% of Wind Speed in a Downwind Direction*
12/16	Oil 2 mi. N to S and 4 mi. E to W; oil moving west streak of oil (bearing about 240°T).	Winds during the morning of 16 Dec. would move oil on a bearing of 245°T.
12/18	Pancakes 27 miles east of ship (090°T). Computed wind drift 3.05%	Maximum movement east, 31 miles, bearing 130°T.
12/20	Main plume 16 miles long bearing 040°T. Computed wind factor 4.00%.	Winds 0900 19 Dec. to 0900 20 Dec. would move oil 14 miles, direction 048°T.
12/21	Maximum eastward movement of oil 53 miles, direction 090°T. Computed wind factor 3.09%.	Maximum eastward movement 60 miles, direction 095°T.
12/22	Maximum eastward movement of oil 95 miles, direction 108°T. Computed wind factor 4.05%.	Maximum eastward movement 82 miles, direction 106°T.
12/23	Maximum eastward movement of oil 86 miles, direction 100°T. Computed wind factor 3.10%.	Maximum eastward movement 97 miles, direction 110°T.

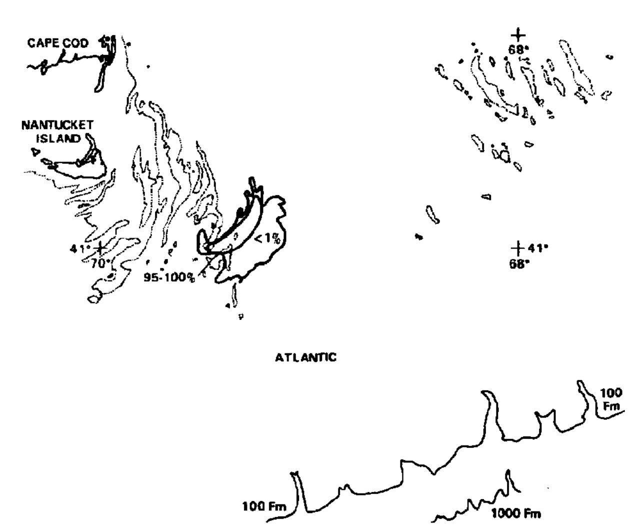

Figure 13. *Observed Area of Oil Spill on 20 Dec.*

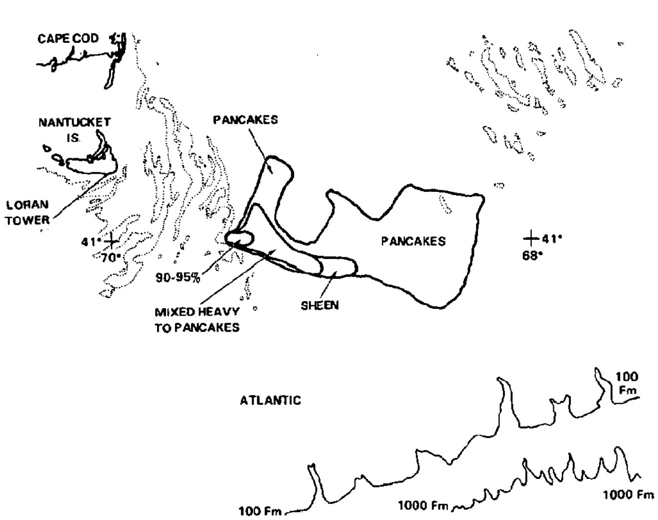

Figure 14. *Observed Area of Oil Spill on 21 Dec.*

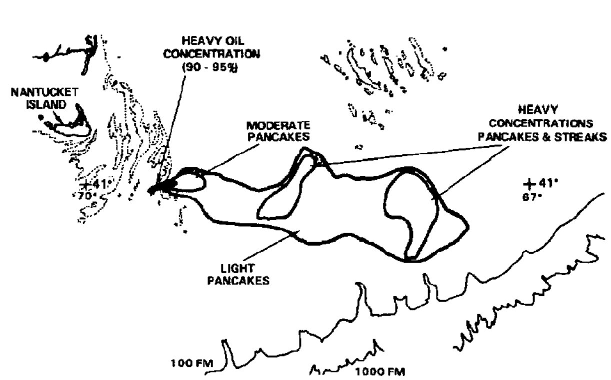

Figure 15. *Observed Area of Oil Spill on 22 Dec.*

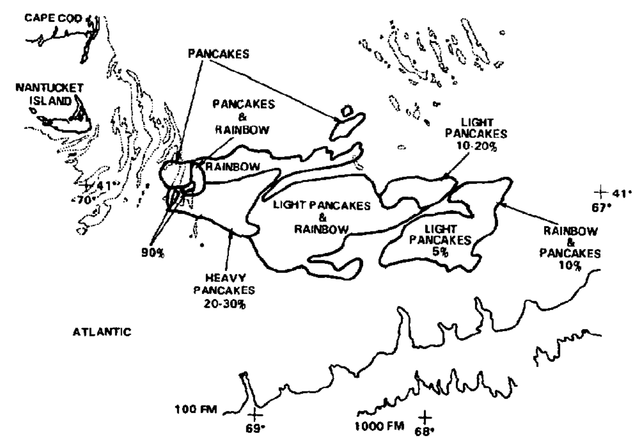

Figure 16. *Observed Area of Oil Spill on 23 Dec.*

20th, the wind factor for the observed movement and the direction of movement of the oil are given in Table 1 on a daily basis. A summary of these values compared to predicted values is shown in Table 2.

One way analysis of variance without replication was performed to determine if statistically significant differences were detectable between observed and predicted wind factor and direction. The analyses are summarized in Tables 3, 4, 5, and 6 respectively.

Conclusions

1. For short-term predictions (i.e., <12 hours) a vectorial addition of wind and tides provided good agreement between the actual direction movement of the oil and the predicted movement as determined from tides and winds. The greatest error occurs in predicting the tidal component for each hour of movement.

Table 2. Comparison of Observed Versus Predicted Movement

Date	Observed		Predicted	
	Wind Factor	*Direction*	*Wind Factor*	*Direction*
12/20	4.00%	040°T	3.50%	048°T
12/21	3.09%	090°T	3.50%	095°T
12/22	4.05%	108°T	3.50%	106°T
12/23	3.10%	100°T	3.50%	110°T

Table 3. Data Array for Wind Factor

Date	*Observed*	*Predicted*	
12/20	4.00	3.5	
12/21	3.09	3.5	
12/22	4.05	3.5	
12/23	3.10	3.5	
	$\bar{x}$ 3.56	$\bar{x}$ 3.5	$\bar{\bar{x}}$ 3.53

2. For quick response answers to where oil will go and when it will get there, vectorial addition of the forces that move the oil is a good method. Use of the 3.5% value for the wind drift factor is of great benefit if no model is available to depict the wind drift current for the area where a spill occurs.

Table 4. ANOVA for Wind Factor

Source of Variation	*Amount of Variation*	*Degrees of Freedom*	*Estimated Variance*	*Observed F Ratio*
Among	0.0072	7	0.0072	
Within	0.8662	6	0.1444	0.0499
Total	0.8734	7		

Conclude that for the 5 percent level of alpha there is no significant difference between the observed and the predicted wind factor.

Table 5. Data Array for Predicted Movement

Date	*Observed*	*Predicted*	
12/20	040°T	048°T	
12/21	090	095	
12/22	108	106	
12/23	100	110	
	$\bar{x}$ 84.50	$\bar{x}$ 89.75	$\bar{\bar{x}}$ 87.13

Table 6. ANOVA for Wind Direction

Source of Variation	*Amount of Variation*	*Degrees of Freedom*	*Estimated Variance*	*Observed F Ratio*
Among	55.13	1	55.13	0.06
Within	5247.75	6	875.63	
Total	5302.89	7		

Conclude that for the 5 percent level of alpha there is no significant difference between the observed and the predicted wind directions.

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Risk Forecasting for the *Argo Merchant* Spill

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Abstract

An oilspill trajectory model, originally developed to assess environmental risks of Outer Continental Shelf oil production, was used during the *Argo Merchant* spill to forecast the risk to various shoreline and marine resources. The model indicated a low risk to these resources given the location and season of the spill and the particular wind conditions under which the spill occurred. Oil from the *Argo Merchant* in fact contacted few of these resources. However, had a spill at this location occurred either under other typical wind conditions for the season or at a different time of year, the model also indicated that risk would have been much higher. Quantitative estimates of risks were constructed assuming different initial conditions, seasons, and durations of spillage.

Introduction

An oilspill trajectory model, originally developed to assess oilspill risks associated with Outer Continental Shelf oil production, was used during the *Argo Merchant* spill to give quantitative estimates of resulting risk of beaching and impacting various resources. The model has been used to assess the risks associated with Outer Continental Shelf oil production in several frontier areas (Slack and Smith, 1976; Slack, Smith, and Wyant, 1977; Smith, Slack, and Davis, 1976a, b). Because the *Argo Merchant* broke up in one of these areas, the data to drive the model had been fully prepared in the region surrounding the grounding site before the incident occurred. Thus, risk forecasts could be made beginning with the first grounding reports.

Risk is defined to be the probability that within a given time spilled oil passes through an area occupied by a shoreline or marine resource at a time of year when the resource is considered potentially vulnerable to oil. In general, for large oilspills, spillage can continue for many days, and oil, once spilled, can persist in observable quantities in the ocean for a considerable period. In either case, spilled oil may contact resources in the vicinity of a spill long after the actual onset of spillage. The model was designed to provide estimates of such long-term risks. It thus serves a different purpose from models developed to provide quick accurate forecasts of imminent movement of a slick based on instantaneous receipt of short-term weather forecasts, current and weather conditions, and the precise state of the slick. Risk arising from the *Argo Merchant* spill was forecast for periods up to 60 days under different assumptions concerning initial wind conditions and spill duration.

The model can be used to answer numerous "special case" questions of interest which inevitably arise in assessing risk from any particular spill or offshore production scenario. As an example, it was unclear at the time of the *Argo Merchant* spill whether considerable amounts of oil might remain in the hull. The question arose as to the time of year to destroy the remaining hull fragments to minimize the risk from the resultant release of oil. The model can provide estimates of risk as a function of spill date as an initial answer to such questions, and was employed for this purpose during the *Argo Merchant* spill.

Description of the Model

The model simulates the movement of hypothetical spills using deterministic ocean currents and stochastically generated winds. In the North Atlantic area, these currents are derived from drift-bottle studies (Bumpus, 1973), and the statistical descriptions of winds are derived from 5 years' record at Georges Shoals and Nantucket Shoals weather towers.

A first-order Markov model for winds is the heart of the risk-forecasting abilities of the model. Historical records of winds for 3-hourly observations are grouped into 41 classes depending on magnitude and direction and analyzed for frequencies of transitions between classes. Given the date and location of a spill, an array of possible future wind patterns on the basis of past wind transition frequencies can be generated. Superimposing the effects of the forces exerted by the ocean currents, winds, and coriolis effect, a hypothetical oilspill trajectory

Table 1. Assumed Seasonal Vulnerability of Resources.
T, assumed vulnerable;
F, assumed not vulnerable

Resource	*Month*											
	Dec.	*Jan.*	*Feb.*	*Mar.*	*Apr.*	*May*	*June*	*July*	*Aug.*	*Sept.*	*Oct.*	*Nov.*
1 Beaches and recreation areas	T	T	T	T	T	T	T	T	T	T	T	T
2 Wildlife sanctuaries and wintering areas	T	T	T	T	T	F	F	F	F	F	F	T
3 Coastal bird breeding areas	T	T	T	T	T	T	T	T	T	T	T	T
4 Pelagic bird nesting areas	T	T	T	T	T	T	T	T	T	T	T	T
5 Pelagic bird wintering areas	T	T	T	T	T	F	F	F	F	F	F	T
6 Eagle and osprey nesting sites	T	T	T	T	T	T	T	T	T	T	T	T
7 Cod and haddock spawning areas	F	T	T	T	T	T	T	F	F	F	F	F
8 Silver and red hake spawning areas	F	F	F	F	F	T	T	T	T	T	F	F
9 Sea herring spawning areas	F	F	F	F	F	F	F	F	F	T	T	T
10 Atlantic salmon migration routes	F	F	F	F	F	T	T	T	T	T	T	T
11 Shortnose sturgeon areas	T	T	T	T	T	T	T	T	T	T	T	T
12 Shellfish areas	T	T	T	T	T	T	T	T	T	T	T	T
13 Harbor seal whelping areas	F	F	F	F	F	T	T	T	T	T	F	F
14 Grey seal whelping areas	F	F	T	T	T	T	T	F	F	F	F	F
15 Salt marshes	T	T	T	T	T	T	T	T	T	T	T	T
16 Eel grass beds	T	T	T	T	T	T	T	T	T	T	T	T
17 Kelp beds	T	T	T	T	T	T	T	T	T	T	T	T
18 Rocky coastline	T	T	T	T	T	T	T	T	T	T	T	T
19 Sandy beaches	T	T	T	T	T	T	T	T	T	T	T	T
20 Nova Scotia	T	T	T	T	T	T	T	T	T	T	T	T
21 Sewage dumpsites	T	T	T	T	T	T	T	T	T	T	T	T
22 Sand and gravel deposits	T	T	T	T	T	T	T	T	T	T	T	T

for each of these samples of wind patterns can be computed. Tabulating the contacts of these trajectories with land or other resources then provides quantitative estimates of the risk to each resource. Because these estimates depend upon the initial conditions under which a spill occurs, the model can be used to assess sensitivity of risk to the location and duration of a spill, the date at which it occurs, and the specific wind conditions under which it occurs.

Risk arising from the *Argo Merchant* spill was forecast for periods up to 60 days. Implicitly, the model provides a pessimistic estimate of risk in that no allowance is made for weathering of oil in that period. However, in model runs elapsed time between oil spillage and resource contact is tabulated, allowing refinement of risk estimates in light of whatever weathering assumptions are desired.

The hypothetical spills generated by the model move in straight lines over each 3-hour time step in the simulation. The direction and distance of the 3-hour movement is calculated as the vector sum of the current and 3.5 percent of the prevailing wind. At each step, the location of the hypothetical spill is checked against a table of resources locations and the simulated date checked against a table of seasonal resource vulnerabilities. Any simultaneous occupation of a one-mile square area by the simulated spill and a resource is tabulated as a contact. Table 1 shows the resources considered and their assumed seasonal vulnerabilities. The locations and seasonal vulnerabilities were estimated by Bureau of Land Management personnel during the oilspill risk analysis for the proposed North Atlantic Outer Continental Shelf production areas (Smith et al., 1976b). Maps of the assumed resource locations appear in that report.

Validity of the Model. The ability of any model to accurately forecast is directly tied to the quality of the driving data. Clearly, wind records from particular sites over finite periods of time do not precisely represent wind patterns to be found at other sites and other time periods; equally clearly, drift-bottle studies imperfectly represent the current patterns of any large area. Unfortunately, little quantitative assessment of the sensitivity of model results to these imperfections can be made; judgments as to the validity of oilspill trajectory model predictions in light of uncertainty in the basic data remain largely a matter of "engineering judgment".

More extensive and precise work has been done investigating the behavior of simple vector addition advection models such as used here for risk forecasts - advection = current velocity + (wind drift factor) x (deflection adjusted wind velocity).

A general review of oilspill trajectory modeling techniques (Stolzenbach et al., 1977) concludes unsurprisingly that such a simple advection model "represents a considerable oversimplification of a very complex process" and discusses a number of potential improvements. However, the review goes on to note that most modelers have found such simple advection equations to be an adequate approximation to the actual advection process. Indeed, the review also points out (section 5, p. 50) that at present most potential improvements to this simple advection model cannot be implemented for models meant to have general applicability; many of the relevant physical processes "have no analytical description available", where analytical descriptions exist, they are often unproven; where proven, there is seldom enough widely available data to make inclusion in a multipurpose model possible.

The review also details laboratory experiments and

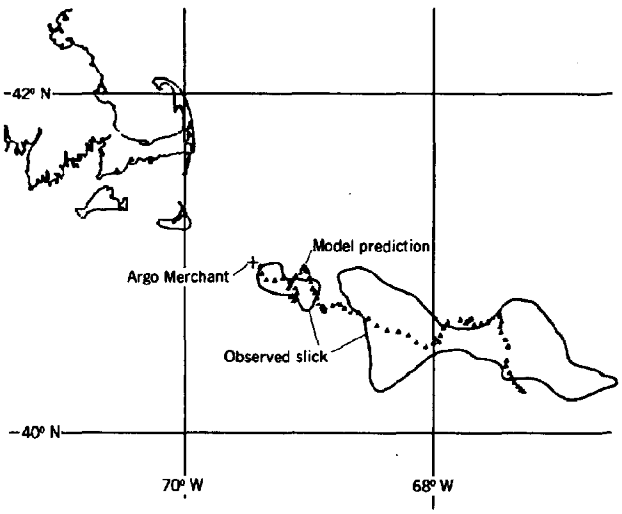

Figure 1. *Model Performance.*

actual ocean observations used to determine appropriate values for wind drift factor and deflection angle for the simple advection models. In varying circumstances, empirically determined values have been reported in a range of 0.008 to 0.058 for drift factors and a range of 0.3° left to 13.2° right for deflection angles (section 3, p. 81). The model used to forecast risk for the *Argo Merchant* spill assumes a drift factor of 0.035 and a deflection angle of 0°. The National Oceanic and Atmospheric Administration preliminary report on the *Argo Merchant* spill (Grose and Mattson, 1977) contains a discussion of the effects of different deflection angle assumptions on performance of the model in tracking the actual spill from the *Argo Merchant.* In the course of the previously mentioned North Atlantic oilspill risk analysis (Smith et al., 1976b), risk was estimated assuming deflection angles of both 0° and 20° to the right. Estimates of risk to shore varied from 0.21 to 0.08 over this range of drift angles. This roughly indicates the sensitivity of the model's risk forecasts to deflection angle assumptions.

The model represents a spill as a point and neglects spreading effects, although resource locations are

Table 2. Risk to Land As a Function of Initial Wind.

Initial wind pattern	*Estimated probability to come ashore*	*Estimated mean days for spills to come ashore*
Initial wind selected randomly from historic winter record	0.10	8
Initial wind northeast 10 knots (reported by USCG, December 16)	0.24	5
Initial wind northwest at 20 knots (reported from *Nantucket Light Ship*, December 17)	0.07	8

Table 3. Risk to Resources As a Function of Initial Wind.
n, less than 0.005; g, greater than 0.995

Resource	*Initial wind selected randomly from historic winter record*	*Initial wind northeast 10 knots (reported by USCG, December 16)*	*Initial wind northwest at 20 knots (reported from Nantucket Light Ship, December 17)*
1 Beaches and recreation areas	0.11	0.24	0.07
2 Wildlife sanctuaries and wintering areas	.11	.24	.07
3 Coastal bird breeding areas	.03	.03	.01
4 Pelagic bird nesting areas	n	n	n
5 Pelagic bird wintering areas	g	g	g
6 Eagle and osprey nesting sites	.01	.02	n
7 Cod and haddock spawning areas	.23	.23	.2
8 Silver and red hake spawning areas	n	n	n
9 Sea herring spawning areas	n	n	n
10 Atlantic salmon migration routes	n	n	n
11 Shortnose sturgeon areas	n	n	n
12 Shellfish areas	.02	.06	n
13 Harbor seal whelping areas	n	n	n
14 Grey seal whelping areas	n	n	n
15 Salt marshes	.01	.02	n
16 Eel grass beds	n	.01	n
17 Kelp beds	n	n	n
18 Rocky coastline	.01	.02	n
19 Sandy beaches	.11	.24	.07
20 Nova Scotia	n	n	n
21 Sewage dumpsites	n	n	n
22 Sand and gravel deposits	.97	.94	.98

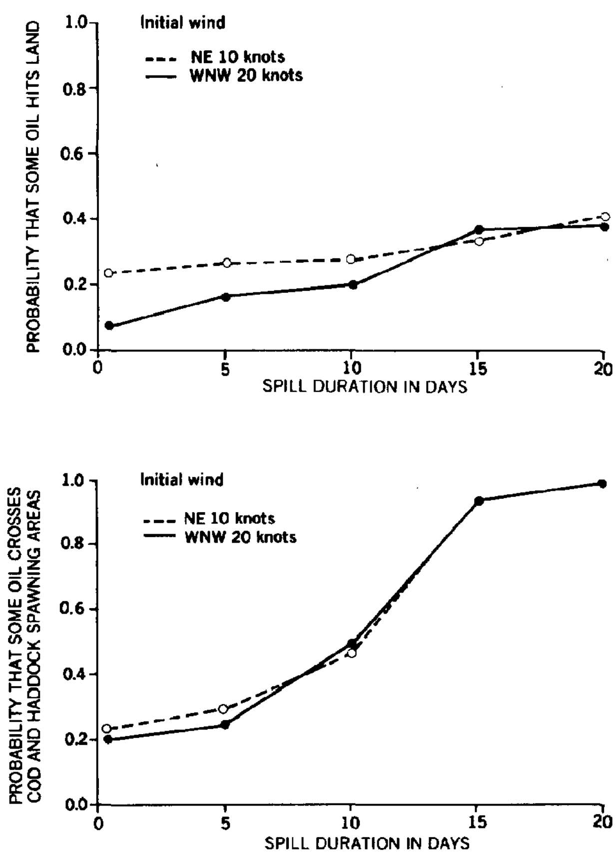

Figure 2. *Risk As a Function of Spill Duration.*

widened in model runs so that any hypothetical spill passing near the actual resource locations will be counted as contact. However, by releasing a number of point spills in sequence and moving them with an identical overall wind at each time step, a 2-dimensional approximate picture of a spill can be generated. Such a picture, using a 0.035 drift factor, a 0° deflection angle, and the 3-hourly winds reported by the *Nantucket Light Ship* from the *Argo Merchant* site, is shown in Figure 1 superimposed on an outline of the actual spill's oil pattern. Such a picture seems to be the best way of communicating the validity of the risk forecasts using the model. It quickly and concisely imparts the level of approximation represented by this model to users of the forecasts who, ultimately, must subjectively assess the worth of the forecasts in consideration of their own needs.

Risk Forecasts

As the *Argo Merchant* began to break up, the model was used to forecast the risk to shore and marine resources from the spill conditional on initial wind conditions. This was done by giving hypothetical spills an observed wind for the first 3-hour time step and thereafter driving them with stochastically generated winds based on the past records. These conditional risk forecasts reflect not only the movement imparted by the wind in the first 3-hour period, but also the past observed persistence of this wind pattern.

Table 2 shows the estimated risk to shore as a function of initial wind; Table 3 shows the estimated risk to resources as a function of initial wind. Each estimate is based on 300 simulated spills assumed to start on December 15. Table 2 shows that there is an estimated probability of 0.10 of impacts to shore from spills occurring in winter at the site of the *Argo Merchant* grounding. For the northwest 20-knot wind reported at about the onset of spillage, estimated risk was even lower. However, had the spill occurred under the northeast 10-knot wind reported one day before the spill actually began, estimated risk to shore would have been 0.24, reflecting the fact that this onshore wind pattern, while unusual in winter, often persists long enough when it does occur to be able to drive oil from the *Argo Merchant* site to shore.

The preceding risk estimates assumed that a spill occurs as an instantaneous release of oil. Figure 2 shows estimated risk as a function of spill duration. These estimates were made by using the model to generate sequences of hypothetical point spills and driving each complete sequence with a common wind at each time step. Thus, each spill of more than 3 hours' duration is simulated as a stream of points such as that in Figure 1.

Table 4. Risk to Land As a Function of Spill Date.

Date	*Estimated probability to come ashore in U.S.*	*Estimated probability to come ashore in Canada (Nova Scotia)*	*Total estimated probability to come ashore*
December	0.10	0.00	0.10
January	.08	.00	.08
February	.14	.02	.16
March	.33	.09	.41
April	.40	.12	.52
May	.33	.34	.67
June	.34	.58	.92
July	.34	.57	.91
August	.29	.38	.67
September	.16	.05	.21
October	.19	.03	.22
November	.21	.01	.22

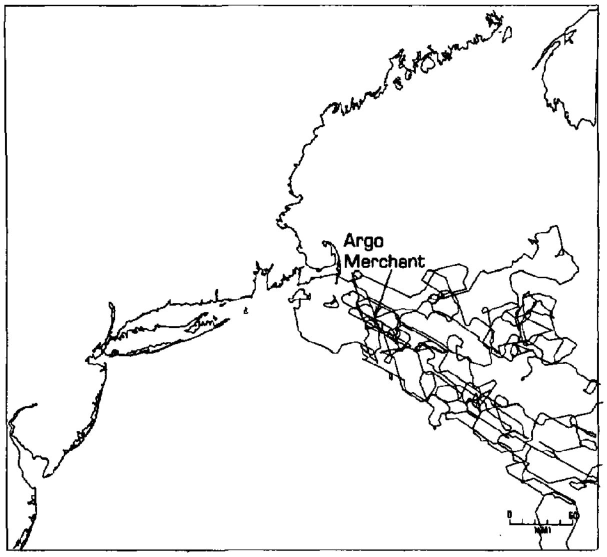

Figure 3. *Simulated Trajectories Winter.*

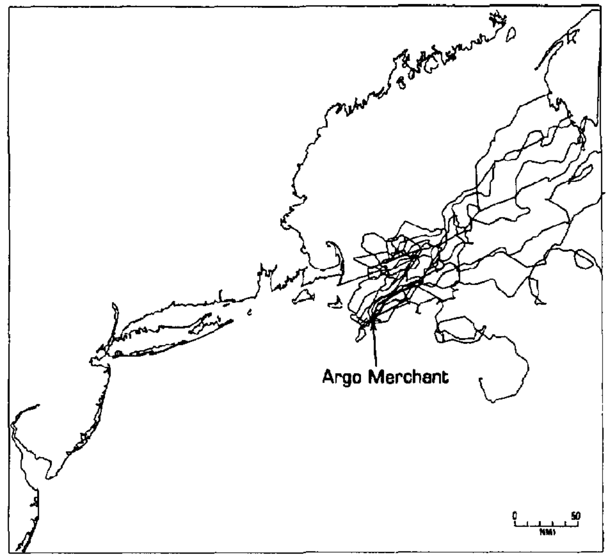

Figure 5. *Simulated Trajectories Summer.*

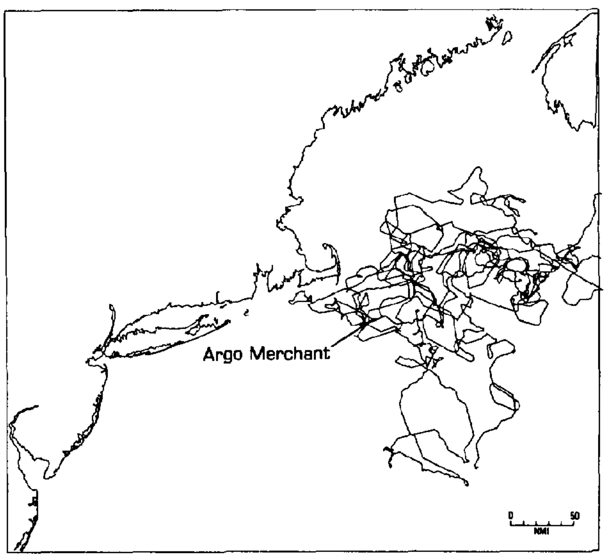

Figure 4. *Simulated Trajectories Spring.*

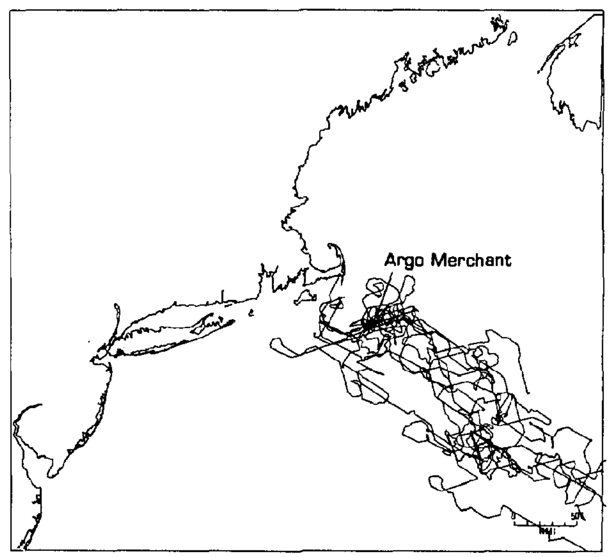

Figure 6. *Simulated Trajectories Autumn*

Estimated risk was defined for this case to be the probability that one or more points of each generated sequence crossed an area occupied by a seasonally vulnerable resource. The estimated probability that some oil from a long spill would reach shore rose to 0.40 for a 20-day spill from the *Argo Merchant* site, and for 15-day spills and up the differences in estimated risk due to different initial wind assumptions disappears. In the model it was assumed that the *Argo Merchant* grounding site was in a cod and haddock spawning area, but that this area was not potentially vulnerable to oil until January 1. The sensitivity of risk forecasts to such assumptions of seasonal vulnerability is also shown in Figure 2; forecasts of risk to cod and haddock spawning areas rose to near certainty for 20-day spills beginning on December 17 from the *Argo Merchant* site.

At one time, it was thought that demolition of lingering hull fragments might be necessary and that such demolition might release some remaining oil. Consequently, risk forecasts for different seasons of spillage were made. Figures 3-6 show 10 simulated trajectories for hypothetical spills from the *Argo Merchant* site in each season. The actual spill followed a path similar to that of the hypothetical slicks in Figure 3. Table 4 shows risk estimates for spills starting from the *Argo Merchant* site for each month. Estimated risk to any shore reaches peaks in June and July and estimated risk to the American shore reaches a peak in April. These estimates clearly supported the natural preference for an early demolition of remaining ship segments should it have been necessary.

Summary

The spill from the *Argo Merchant* was driven southeast and out to sea, passing through fishing areas but not contacting shore resources to any appreciable extent. A risk forecasting model predicted this to be the most likely path for this spill, given the location and season and the particular wind conditions under which the spill occurred. However, the model's risk forecasts indicated that, had a spill at this location occurred either under other typical wind conditions for the season or at a different time of year, risk would have been much higher.

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Near-Bottom Transport in the Vicinity of the *Argo Merchant:* A Seabed Drifter Study

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Abstract

Seabed drifters were released from early January through March, 1977, by helicopter and ship in an area bounded by latitude 40°N. and 42°N. and longitude 67°W. and 72.5°W. to determine the possible transport of *Argo Merchant* oil by near-bottom currents. A total of 176 of the 1800 drifters released were recovered as of December 1, 1977. Of these, only 38 are known to have been recovered intact. Ship-launched drifters released at University of Rhode Island (URI) stations 8 and 9, located 8 nautical miles south southwest of the wrecksite and at the *Argo Merchant* site, respectively, had the largest number of intact drifter returns. Based on a 12 percent return from these stations there appears to be a near-bottom drift component to the northwest. These results corroborate the findings of Bumpus (1973) in this area. Drift rates of 0.3 - 0.6 nautical miles/day are similar to those reported by Bumpus (1973). Only three drifters released east of longitude 69°W. were recovered suggesting a divergence of near-bottom drift in this area with an offshore component to the east of 69°W.

Background and Previous Studies

An immediate concern after the grounding of the *Argo Merchant* was that the No. 6 fuel oil carried by the tanker would sink to the bottom, contaminate the sediments, and be transported towards Massachusetts and Rhode Island shores. The specific gravity of heavy residual fuels, such as that carried by the *Argo Merchant,* may increase as a result of evaporation of volatile components, allowing the oil to sink to the bottom (Grose and Mattson, 1977; p. 66). Determinations of the physical properties of the cargo oil from the *Argo Merchant* by J. H. Milgram (Grose and Mattson, 1977; p. 71) revealed the specific gravity of the No. 6 oil to be 0.96, not the value of 0.996 reported by the U.S. Coast Guard. This early finding, indicating the oil would not sink, was based on distillation results, and was not considered conclusive evidence that the oil would not sink. Several processes which may cause oil to sink include: 1) loss of soluble low molecular weight components by weathering, 2) adsorption of oil onto sediment increasing the density, and 3) direct physical mixing of the oil into the sediments by turbulence. It is now estimated that less than one percent of the *Argo Merchant* oil reached the bottom (Hoffman and Quinn, 1978). If *Argo Merchant* oil had sunk to the bottom, it could have drifted to the northwest based on seabed drifter studies of near-bottom circulation on the continental shelf showing that from the Great South Channel to south of Rhode Island, the predominant near-bottom drift direction is to the northwest at a rate of 0.7 ± 0.2 nautical miles/day with a transport tendency toward the mouth of Narragansett Bay (Bumpus, 1973).

Drifter returns of earlier releases in the vicinity of the *Argo Merchant* are about 10 percent (Bumpus, 1973), suggesting a substantial offshore drift component (Bumpus, 1976). To the west of Nantucket Shoals the returns are substantially greater. In general, Bumpus (1973) notes a divergence of near-bottom flow, with an inshore drift component landward of the 50 meter contour and an offshore tendency seaward of this line.

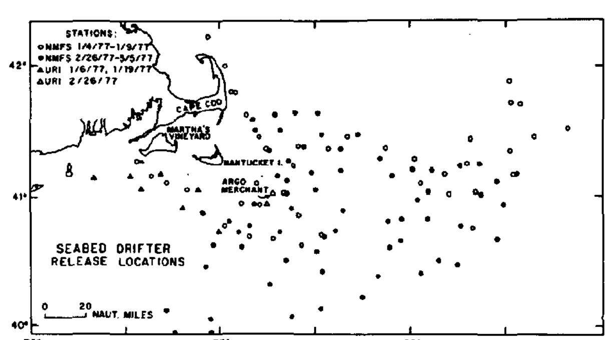

Figure 1. *Seabed drifter release locations in the vicinity of the Argo Merchant.*

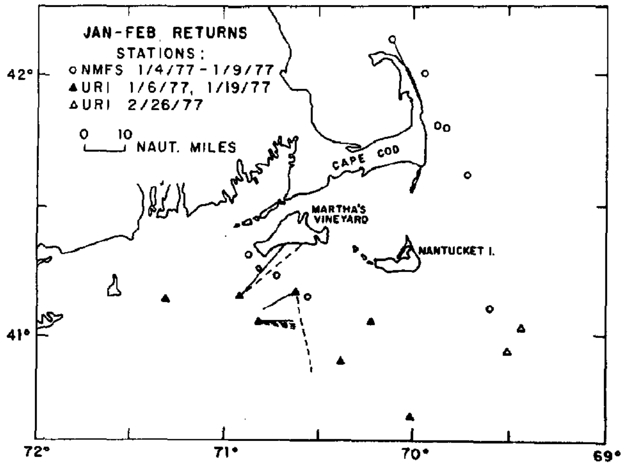

Figure 2. *January through February, 1977, seabed drifter returns in the vicinity of the Argo Merchant. Solid lines show inferred travel paths of all drifters that were recovered broken or whose condition is unknown. Dashed lines show inferred travel paths of all drifters known to have been recovered intact.*

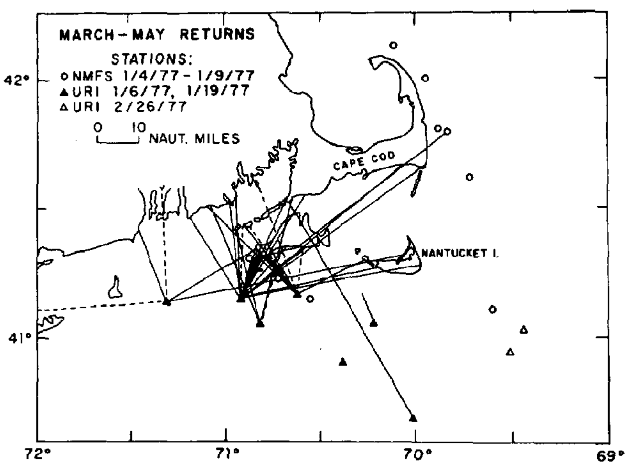

Figure 3. *March through May, 1977, seabed drifter returns.*

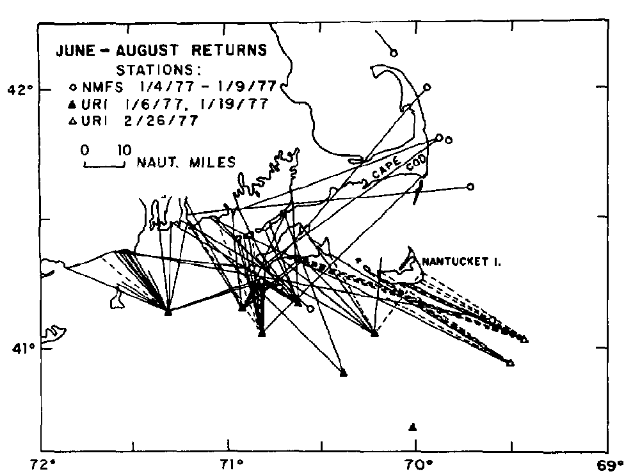

Figure 4. *June through August, 1977, seabed drifter returns.*

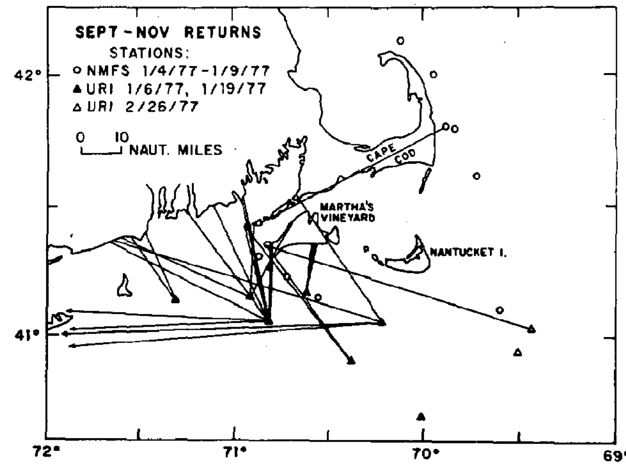

Figure 5. *September through November, 1977, seabed drifter returns.*

The University of Rhode Island and the National Marine Fisheries Service (NMFS) of Woods Hole deployed approximately 1800 Woodhead type seabed drifters (Lee et al., 1965) over Nantucket Shoals, Georges Bank, and Rhode Island Sound to determine the possible transport direction of any oil from the *Argo Merchant* that sank to the bottom (Figure 1). A total of 1150 drifters were released by helicopter and ship at 9 URI stations and 535 released during two NMFS cruises. Bundles of 75, 100, or 150 drifters were deployed at the URI stations and groups of 5 at each NMFS station. Clusters of drifters were weighted for rapid descent to the seafloor where a water soluble link dissolved in about ten minutes, releasing the drifters to respond to near-bottom currents.

Results and Discussion

During the period from January 6, 1977, to December 1, 1977, approximately 10 percent of the drifters were recovered. Of the total of 176 returned, 84 are known to have lost their stems and weights. When this occurs the drifter loses its negative buoyancy and becomes a surface drifter. The plastic drifters, purchased from Insul-Tab in Woburn, Massachusetts, may have become brittle in the cold waters and broken apart as they moved through the surf zone. Follow-up letters confirm that only 38 of the drifters were found intact; the condition of the remaining 54 is not known.

A seasonal analysis of the recovery data (Figures 2 - 5) shows a 5 percent return in January and February increasing to 25 percent in March through May. The return maximum of 44 percent in June through August (Figure 4) falls off rapidly to only 14 percent in September, October, and November. The three-month recovery plots show that although the majority of the drifters were recovered broken, the predominant direction of drifter movement was the same as the intact seabed drifters. During December, January, and February the wind direction is predominantly from the northwest (Grose and Mattson, 1977; Morgan and Anthony, 1977). Therefore, if the drifters had broken apart at some time before stranding, an offshore direction of travel would be expected. Although the quality of the data is poor, there appears to be a change from a predominantly northeastward drifter movement during March through May to a strong northwestward drift in June, July, and August.

Of the total released, 150 drifters were deployed on February 26, 1977, at URI stations 8 and 9, located 8 nautical miles south southwest of the wreck and at the *Argo Merchant* site, respectively (Figure 1). These were ship-launched and have the largest number of intact drifter returns, 13 complete of the 18 returned. Based on a 12 percent return from these stations there appears to be a component of near-bottom drift to the northwest. These results corroborate the findings of Bumpus (1973) in this area. The first drifter recoveries from the two stations did not occur until mid-June with the majority recovered in July. Drift rates of 0.3 - 0.6 nautical miles/day calculated for stations 8 and 9 are similar to the rate of 0.7 ± 0.2 nautical miles/day found by Bumpus (1973) from Great South Channel to south of Rhode Island.

Only three drifters released east of longitude 69°W. were recovered suggesting a divergence of residual drift in this area. Bumpus (1976) notes an offshore drift on Georges Bank based on low drifter returns from this region. Great South Channel, approximately delineated by the 69°W. longitude line, may convey many of the drifters from both Nantucket Shoals and the western portion of Georges Bank offshore.

Conclusions

Residual bottom drift in the area of the *Argo Merchant* appears to be primarily offshore with a small onshore component of drift to the northwest. Results from this study corroborate Bumpus' (1965, 1973, 1976) findings of a minor northwest drift component transporting drifters at a rate of less than one nautical mile/day. Higher recovery rates and drift speeds are observed for drifters released closer to shore. There appears to be a divergence of residual bottom drift associated with the Great South Channel.

Although little *Argo Merchant* oil appears to have sunk to the bottom, heavy residual fuels such as the fuel oil carried by the *Argo Merchant* have been known to sink as the lighter volatile components evaporate. Seabed drifter studies appear to be a valuable technique to determine possible transport routes of oil spills that reach bottom. However, the usefulness of the present results are severely limited because at least half of the recovered drifters broke apart. The design and quality of materials used in the construction of seabed drifters should be evaluated further to insure drifters will remain intact throughout the study.

Acknowledgments

This study was partially funded by NOAA Contract 03-7-022-35123.

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Surface and Subsurface Spill Trajectory Forecasting: Application to the *Argo Merchant* Spill

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Abstract

In an effort to meet the needs of the coastal zone management community and the University of Rhode Island oil spill response team in planning for oil spill response, trajectories were forecast for the Argo Merchant spill. Using a simple surface drift model, the spill trajectory was estimated for periods up to 30 days. Actual spill motion closely followed the predicted mean trajectories. Based on the seabed drifter data of Bumpus, a simple advective model was constructed to estimate possible subsurface oil transport trajectories. The results of the model agree qualitatively with seabed drifter studies performed during the spill.

Introduction

Shortly after the *Argo Merchant* ran aground in the Nantucket Shoals area, requests were made to the Ocean Engineering Department by the Rhode Island coastal management community, the University of Rhode Island Oil Spill Response team, and the governor of Rhode Island's energy advisor to provide probable oil spill trajectories. This information was needed in order for the Rhode Island community to develop an appropriate oil spill contingency plan.

To meet this need, two simple computer models were constructed — one to predict the surface drift of spilled oil, while the second predicted the subsurface drift patterns. The results of this effort are presented here.

Surface Drift Model

In the simple surface drift model that was developed, it was assumed that the wind induced a surface drift of 3.5% of the wind velocity. This drift is accounted for by 1.5% for the wind induced water motion and 2.0% for the relative oil/water motion (Smith, 1974). It was further assumed that the wind induced surface drift was in the same direction as the wind.

The model was run using two-hour time steps, i.e., the spill was moved at the determined rate and in the

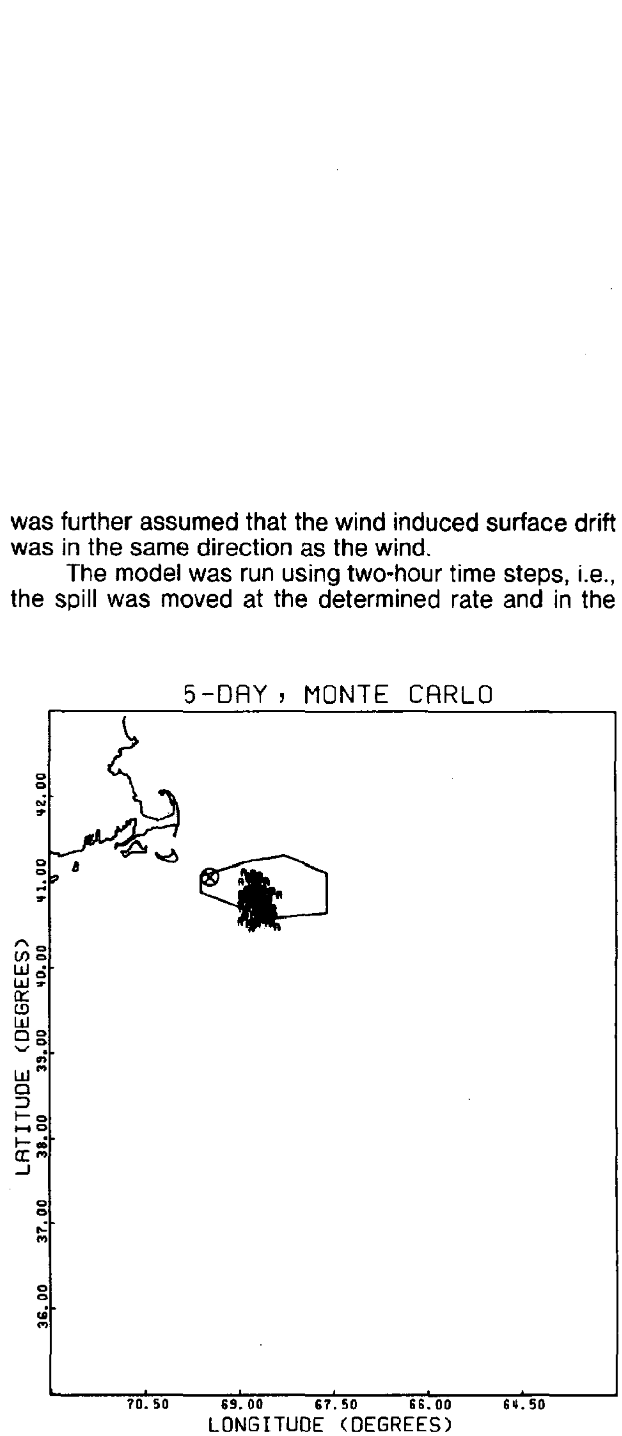
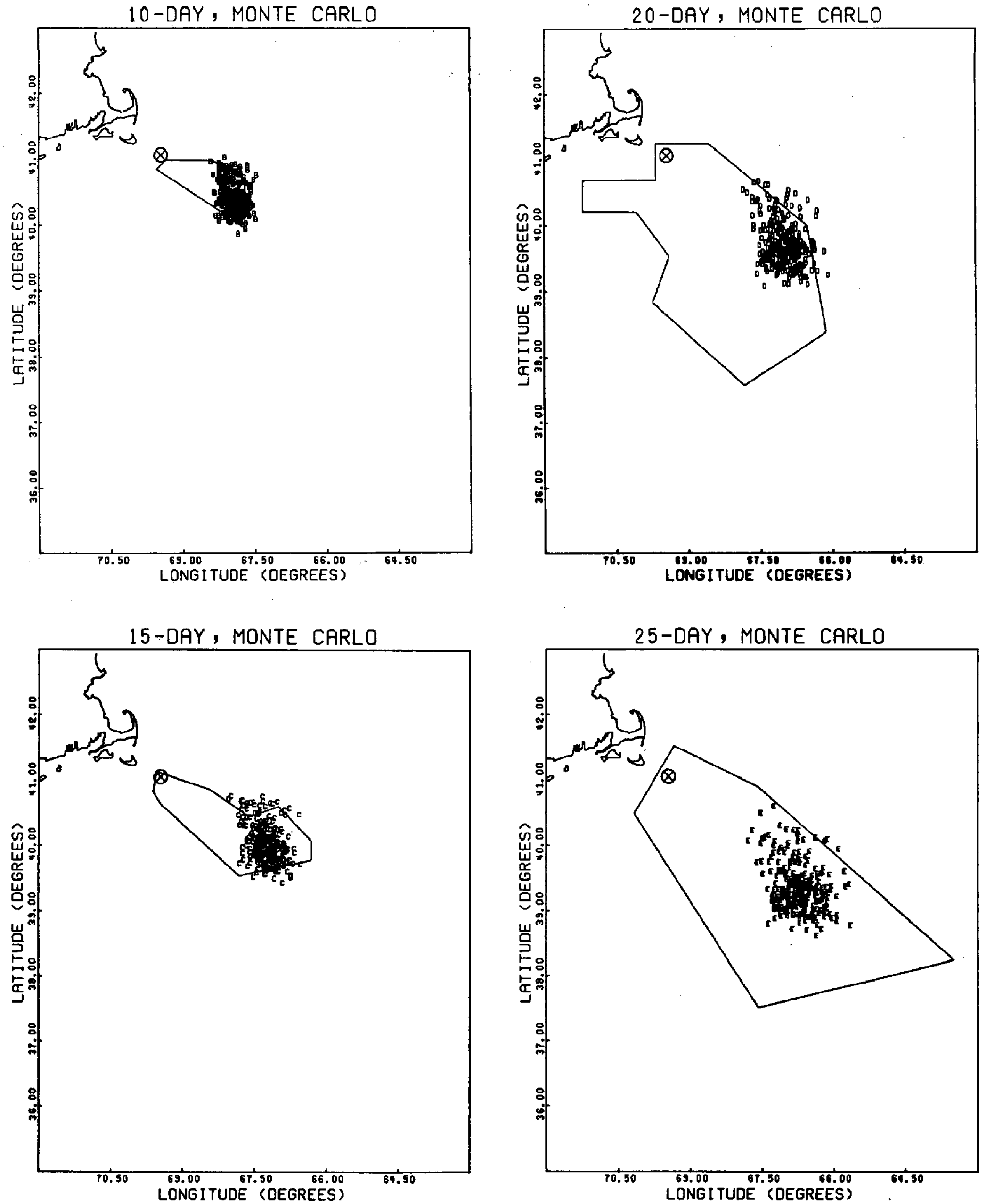
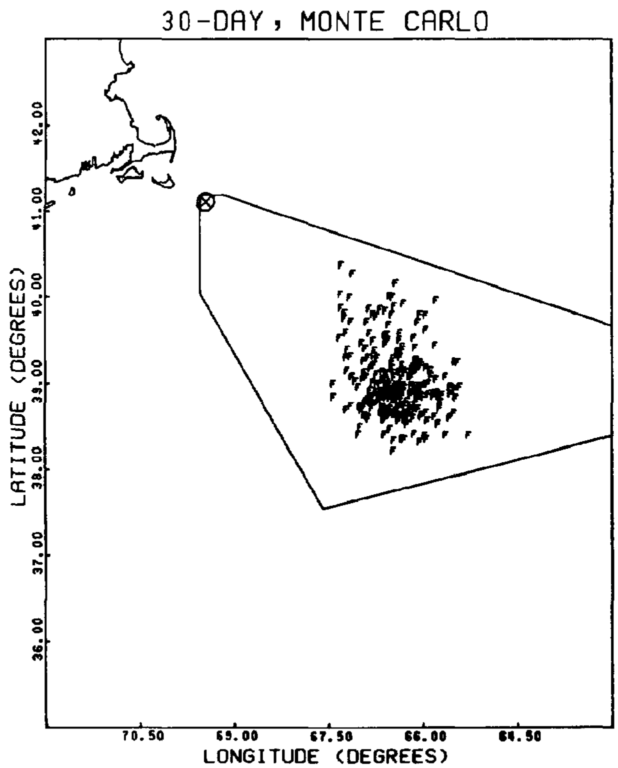


Figure 1. *Monte Carlo surface drift predictions (wind & tidal currents) for 5, 10, 15, 20, 25, 30 days after the spill.*



determined direction for a period of time corresponding to two hours before the wind was changed. The necessary wind data was obtained from the Grant Point Coast Guard Station on Nantucket Island. Tidal currents were taken from the National Oceanic and Atmospheric Administration Navigation Chart 13006. All cases were run starting on December 18 and calculated 30-day trajectories.

Monte Carlo runs were made both for wind-driven



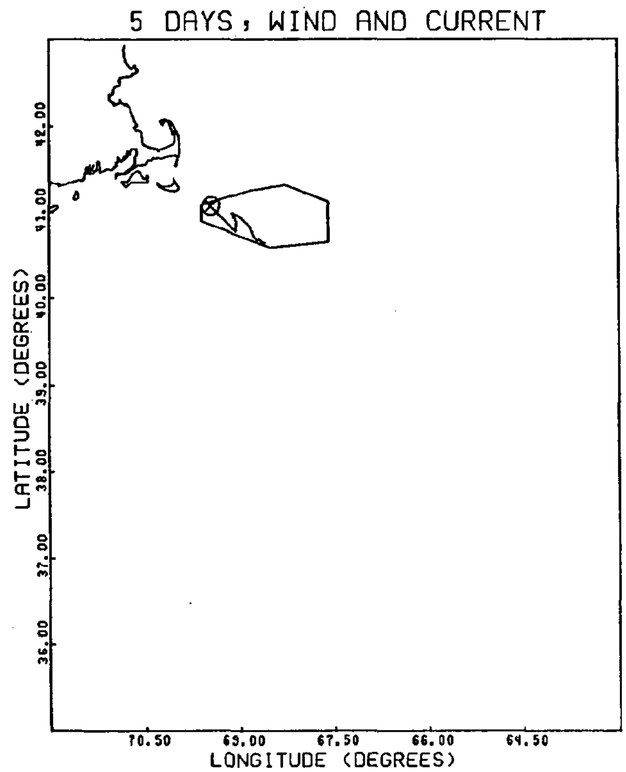
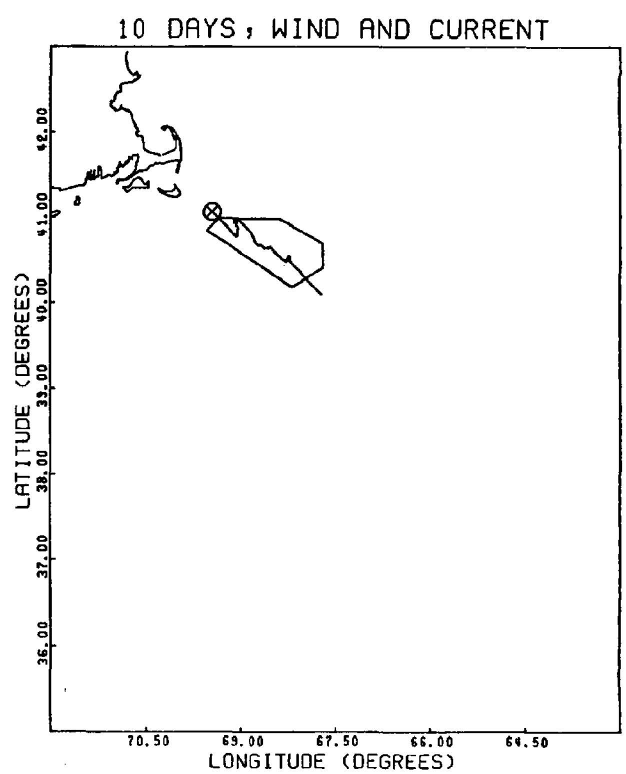


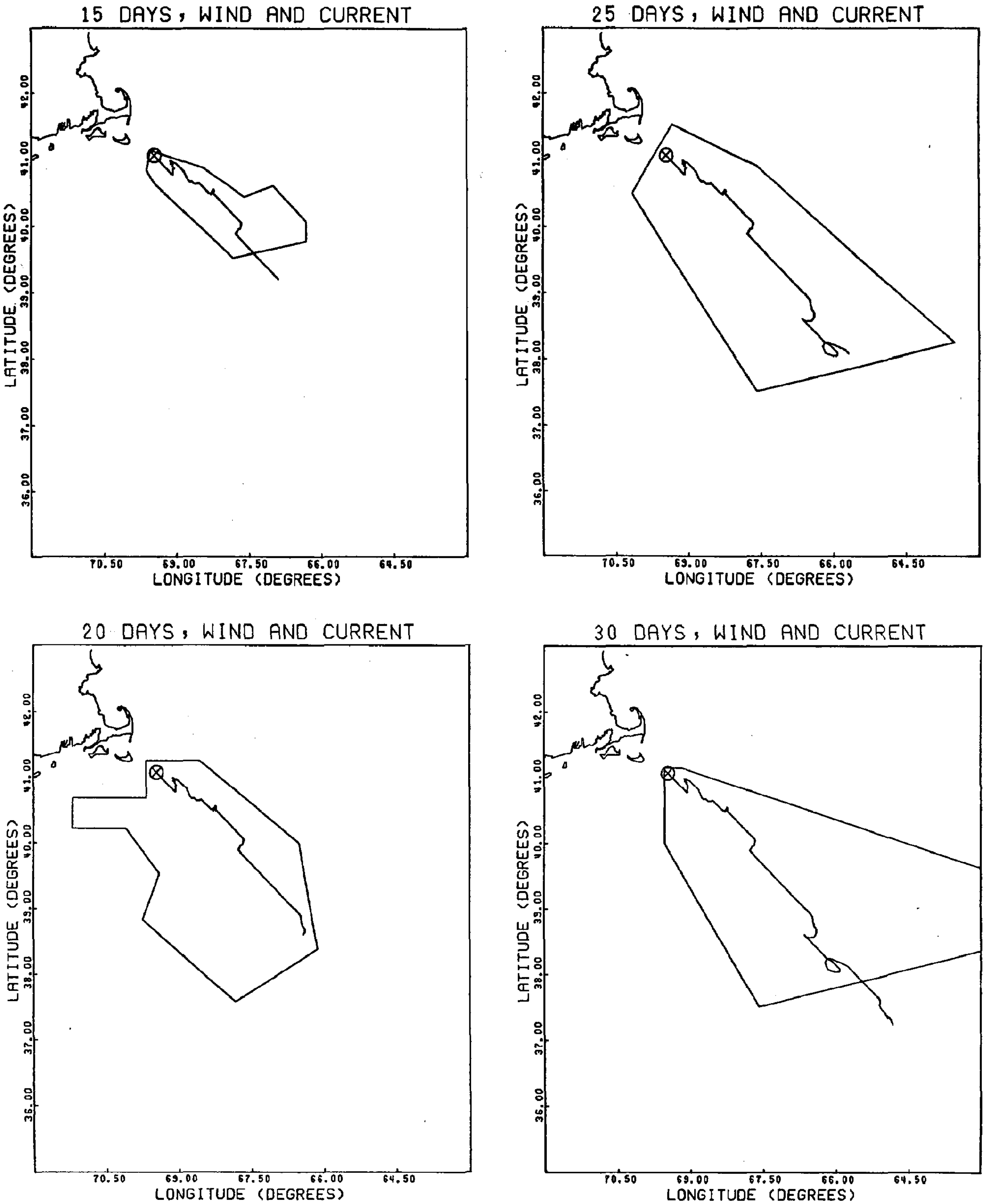
Figure 2. *Deterministic surface prediction (wind & tidal currents) - 5, 10, 15, 20, 25, 30 days after the spill.*

currents and for wind-driven currents added vectorially to the local tidal currents. The wind speed and direction for the Monte Carlo runs were randomly sampled such that the probability of obtaining a given wind magnitude and direction equals the probability that such conditions are observed in the appropriate month during the past ten years. This ten-year averaged data (U.S. Naval Weather Service Command, 1970) lists the probability by month of obtaining the wind velocity in each of six speed ranges for each of eight wind directions. Once a direction and magnitude were chosen for the wind, the wind induced drift of the oil was calculated and vectorially added to the tidal current. Net nontidal surface drifts were not included because of a lack of information. The slick was then moved at the prescribed drift rate for two hours at which time the procedure was repeated. Figure 1 represents the 5, 10, 15, 20, 25 and 30-day Monte Carlo predictions corresponding to 200 trajectories in which the tidal currents have been included.

Similar runs were made for the case of wind induced currents only, and the results are almost identical to those for the combined wind induced drift and tidal currents (Noll, Cornillon, and Spaulding, 1977). As expected for the strong winds characteristic of the winter in the area, and the long duration of the predictions relative to the tidal period, the wind induced drift dominates the advection of the spilled oil.

In an effort to assess the performance of the simple trajectory model, a deterministic hindcast of the spill location based on actual wind measurements at the site was made as the data became available. Figure 2 presents the results of this simulation compared to observations on the slick boundary, provided by Richard Giggs of the U.S. Coast Guard, in five-day intervals for a month.





The U.S. Naval Weather Service wind data for the Quonset region indicates that the westerly and northwesterly winds predominate. This yields a general east-southeast movement of the oil slick. The trajectories calculated by both models follow the direction of the actual slick reasonably well until the 25-30 day period. At that time, the trajectories continue on their east-southeast path while the slick assumes an almost due

Table 1. Summary of residual bottom drift literature for southern New England shelf

Reference	Observation Location	Observation Length	Type of Observation	Residual Bottom Drift (cm/sec)	Drift Direction	Comments
Beardsley & Butman (1974)	40°45'N 71°03'W 18 m from bottom (60m depth)	March 8-April 10, 1974	Richardson Type Current Meter	6.2	Westward (Along Shore)	Two Northeast Storms (Lasting a Total of 4 Days) Produced 2/3 of Net Westward Displacement Observed During the Experiment
Bumpus (1973); also see Saila (1973)	Cape Cod to Cape Henlopen	1961-1970	Sea Bed Drifters	1.4± .4 Great South Channel to South of R.I. .2 - 1.4 but more frequently .4 - 1.0	Offshore of a Line Drawn about 1/2 to 3/4 of Distance Between the Shore and the 50 Fathom Contour at Depths of 30-35 Fathoms, the Tendency is Toward an Offshore Drift. Inside this Line, the Tendency is for the Flow to be Westerly or Southerly with a Component Toward the Coast	Drift Toward Mouth of Estuaries, Particularly Evident South of Rhode Island

east heading. This marked change in direction by the slick from the wind induced drift could be considerably improved by addition of Gulf Stream generated currents.

Subsurface Drift Model

Since all the preliminary information we could obtain at the time indicated that *Argo Merchant* oil had a high specific gravity, .96 (Grose and Mattson, 1977), and it appeared that the suspended sediment concentrations would be extremely high due to the high wind and wave environment and shallow depths of the spill site, the possibility for oil sinking, either by itself or attached to sediment particles, and being advected along with the bottom currents was considered.

A simple advective transport model was developed to predict probable trajectories if the oil were to be transported by bottom currents. In an effort to provide estimates of bottom drift direction and speeds, a quick review of the literature was undertaken and revealed several investigations on seabed drifter studies and current meter measurements on the southern New England shelf. These studies are summarized in Table 1.

Using the inferred bottom drift directions and

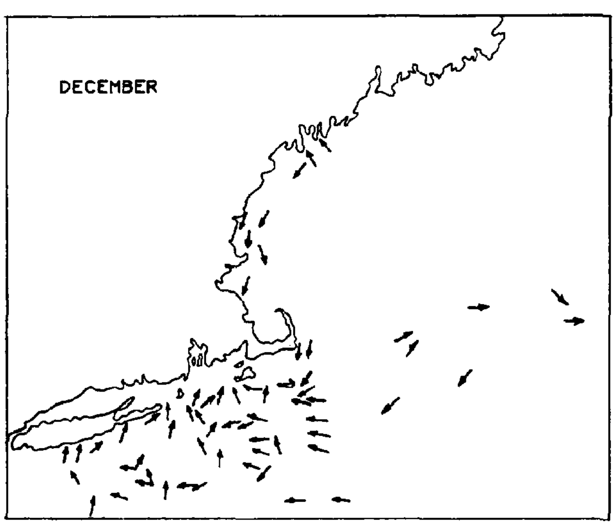


Figure 3. *Inferred bottom drift for December, 1961-1970 (Bumpus, 1973).*

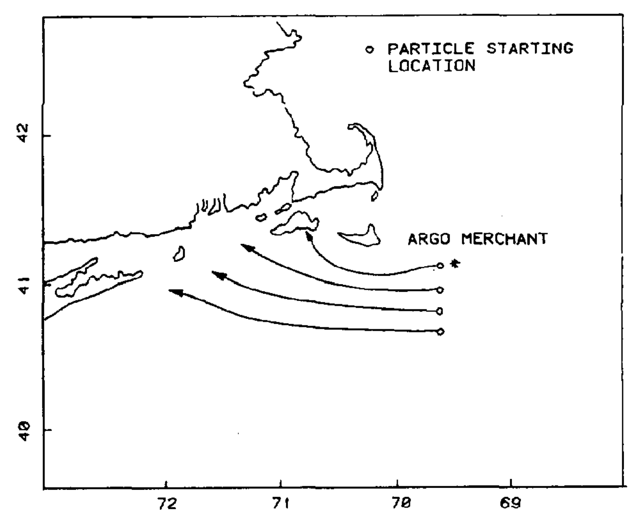


Figure 4. *Bottom drift trajectories based on Bumpus (1973) seabed drifter data.*

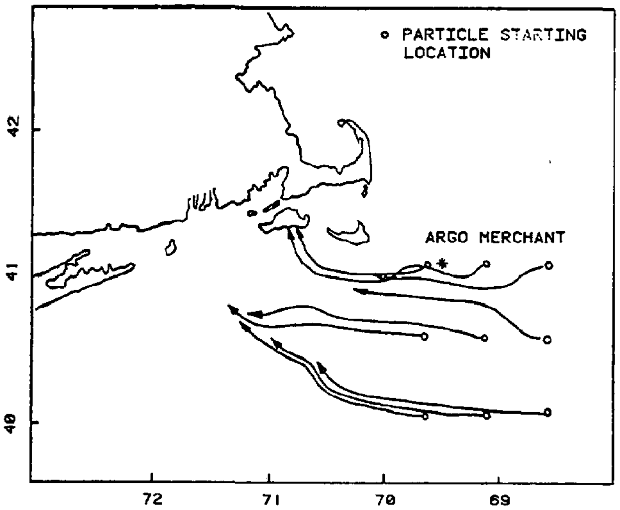


Figure 5. *Bottom drift trajectories based on Bumpus (1973) seabed drifter data.*

speeds for December based on Bumpus' (1973) review of the 1961-1970 seabed drifter data, as shown in Figure 3, several bottom drift trajectories were predicted. Simulated oil particles were started from several locations in the area of the spill; also, the path of the surface slick and trajectories were simulated using a one-day time step. Advective velocities for the oil particle were determined by taking the closest velocity to the particle at each time step. Figures 4 and 5 display typical bottom drift trajectories.

These figures clearly show a bottom drift toward Rhode Island's coastal waters. Employing the several estimates for bottom drift speed, noted in Table 1, estimates for time of arrival of oil particles at shore would be 30-150 days after entrainment in the water column. Comparison of these trajectory estimates with the seabed drifter study performed by Collins, Griscom, and Hoffman (1978) in the area of the spill show good agreement.

Summary

The rapid development and application of these simple computer models to predict both surface and subsurface drift of the *Argo Merchant* oil spill proved to be very beneficial to the Rhode Island management community in planning spill response efforts as well as to the URI Oil Spill Response team in planning the initial oceanographic cruises. While the surface drift predictions were adequate for planning purposes, much work remains to be done in order to predict the fate of oil discharged into the marine environment.

Acknowledgments

Financial support for this effort was provided by ERDA Contract DY-76-S-02-4047. Valuable contributions in developing and coding the computer programs and data were provided under severe time constraints by Dr. P. Cornillon, C. Noll, and R. Gordon of the Ocean Engineering Department at the University of Rhode Island. Computer facilities were furnished by the URI Academic Computer Center.

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Oil Droplet Measurements Made in the Wake of the *Argo Merchant*

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Abstract

In an attempt to determine the size of entrained oil particles following the *Argo Merchant* spill, one liter water samples were filtered and the resulting filters examined for signs of oil. The technique used was similar to that used by Forrester following the grounding of the Tanker *Arrow*. In the case of this spill only several fairly large (>100 μ) oil particles were detected in all of the samples examined. The scarcity of observed oil is most likely a result of the high rate of dispersion of entrained droplets, if any, the observational difficulty resulting from large sediment and biological concentrations in the water and the fact that the bulk of the samples were obtained approximately seven weeks after the *Argo Merchant* broke up and long after the surface spill had left the area.

It was possible, however, to obtain interesting results with regard to the structure of 100μ and greater droplets specifically whether or not they contained sediments. Three general droplet structures were identified:

1. Pure oil with no sediments in or adhering to the droplet;
2. A large oil droplet, between 100μ and 500μ, with small particles of sediment inside; and,
3. A large piece of sediment, between 100μ and 500 μ coated with oil.

Those samples with droplets falling in class 1 were taken from the surface (bucket samples) or one meter below the surface (Nisken bottle). Those samples with droplets falling in classes 2 and 3 were taken at 6 meters and a meter above the bottom.

Introduction

The objective of the experimental work described herein was to measure the droplet size distribution of entrained oil in the 1μ to 100μ range under actual spill conditions. Unfortunately this effort was unsuccessful due to the large number of microorganisms and the high sediment load in the water at the time. Interesting results relating to the structure of larger oil droplets, 100μ to 500 μ, were obtained, and these along with the reasons for attempting the droplet size measurements, the apparatus and experimental technique used and the problems encountered are discussed below.

Why Make the Measurement? The first question which comes to mind is why should one want to make such a measurement (oil droplet size distribution) rather than simply relying on the values of concentration obtained through chemical analysis which are more easily made and more accurate? The main reason is that the shape and mean value of the oil droplet size distribution define a set of variables which are extremely important in determining the fate of entrained oil. Some of the more important physical and biological processes affected by this distribution are:

1. *Residence time in the water column.* This refers to the length of time for which a droplet will remain submerged. This time determines the distance that the droplet is advected as well as the distance that it diffuses which, for a cloud of entrained droplets, defines the areal extent of the cloud and its center of mass as a function of time. The residence time also affects the probability that a droplet finds its way to the bottom.
2. *Rate of biological consumption.* Current theory indicates that the rate of microbiological consumption depends critically on the oil-water interfacial area rather than simply on the concentration of oil (Traxler and Bhattacharya, 1977).
3. *Suspended sediment/oil droplet interaction.* The size of an oil droplet will most likely affect the probability of its adhering to or absorbing suspended sediments. The size of the droplet will also determine whether or not it remains buoyant when and if it sticks to a given piece of sediment. A decrease in buoyancy may lead to the sinking of the droplet or to a substantially longer residence time in the water column.

Those of us at the University of Rhode Island working on the use of chemical dispersants with oil spills are especially interested in the droplet size distribution because the primary functions of a dispersant are to promote entrainment and to increase the stability of the oil-in-water dispersion, therefore enhancing the impact of the above processes on the fate of spilled oil.

How May the Measurement Be Made? Several approaches have been taken in the past to measure the oil droplet size distribution in the water column. These are briefly outlined below.

a. *Use of a Coulter Counter.* The Coulter Counter is an electronic instrument which measures the oil droplet size distribution directly. This is done by forcing the oil-in-water dispersion through a narrow orifice and inferring the size of each oil droplet from the change in capacitance of the water as that particular droplet moves through the orifice. The technique suffers from two major disadvantages for actual oil spill work.

i. It cannot distinguish between oil droplets and microorganisms.

ii. The flow rate is low because of the narrow orifice, thus making the sampling of large volumes of sea water an extremely lengthy process.

In open ocean spill work the number of oil droplets per liter is so low (<100/liter) that the two problems mentioned above render the technique impractical. Coulter Counters have, however, been used quite effectively in the laboratory.

b. *Counting the Oil Droplets in a Drop of Water Using a Microscope.* To determine the droplet size distribution using this method (Jasper et al., 1977) a drop ($\simeq$ .025 ml) of the oil-in-water dispersion is examined under a microscope. The oil droplets in the dispersion are measured and counted. This method is quite straight-forward but the analysis time for a small volume (a few milliliters) of the dispersion is extremely long. Furthermore sediment particles often resemble oil droplets. For small numbers of droplets per liter (<10^5) these two problems make this method impractical.

c. *Filter the Oil-in-Water Dispersion and Count Droplets on the Filter.* This technique was first used by Forrester (1971) for the *Arrow* spill. The procedure involves filtering the oil-in-water dispersion through a millipore filter and then examining the filter under a microscope. A fairly large volume of the dispersion, one liter say, may be filtered in several minutes and then because the area of the filter is small (<10 cm^2) the entire filter may be scanned rapidly for oil droplets. In this way even a very small number of oil droplets per liter is readily detectable. One disadvantage with this approach is that the area of a droplet on the filter must be correlated with the diameter of a droplet in suspension. Another problem is that small oil droplets (<100 μ) are very difficult to distinguish in water containing high concentrations of suspended sediments and/or microorganisms.

Methods

Experimental Apparatus. For this project the filtering technique described above was selected. The main reason being that the results of Forrester indicate a very low concentration of suspended oil droplets for a spill quite similar in nature to the *Argo Merchant,* thus ruling out the other two methods.

Several iterations were performed in the actual experimental set-up before the apparatus described below was finalized. This set-up was used on the last two cruises of the R/V *Endeavor* to the site of the *Argo Merchant,* cruises EN-004 and EN-005. On the first two cruises EN-002 and EN-003 the concept was the same but the experimental set-up was somewhat different.

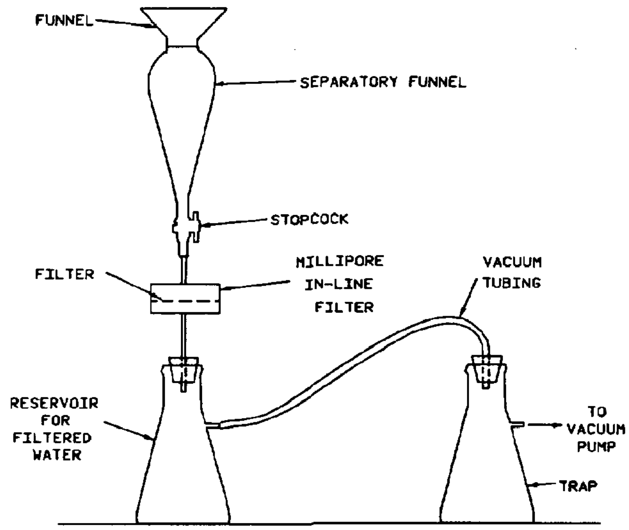

Figure 1. *Experimental apparatus.*

A schematic of the filtering apparatus is shown in Figure 1. Although this figure shows only one in-line filter with the associated glassware, there were actually three such assemblies each leading to the same vacuum trap. In this way it was possible to filter three different samples simultaneously. This approach was selected because the data collection procedure used generally provided three water samples, the first taken approximately one meter below the surface, the second taken approximately six meters below the surface and the third taken approximately one meter above the bottom. From 500 to 1000 milliliters of sea water were filtered through the millipore filters with the pore size ranging from .8 μ to 8 μ.

Results

To begin with, the objective of the experiment, to measure the oil droplet size distribution in the 1 μ to 100 μ range, was not met. This was primarily due to the fact that at most locations the large sediment load and the large number of microorganisms made it impossible to determine whether or not there were any oil droplets less than 100 μ on the filter. Oil droplets larger than 100 μ were detectable however and the distribution of samples with such droplets is discussed below.

R/V Endeavor Cruise EN-002. On this cruise, due to the bad weather only several samples were taken. Only one oil droplet was detected, this in a sample taken approximately 30 kilometers east-southeast of the *Argo Merchant* wreck. This droplet was irregular in shape and measured approximately 100 μ by 300 μ. It was dissolved with carbon tetrachloride and showed no sediment inside of it. A photograph of the droplet is shown in Figure 2 as seen through a microscope under the magnification X100. The results of the analysis of the

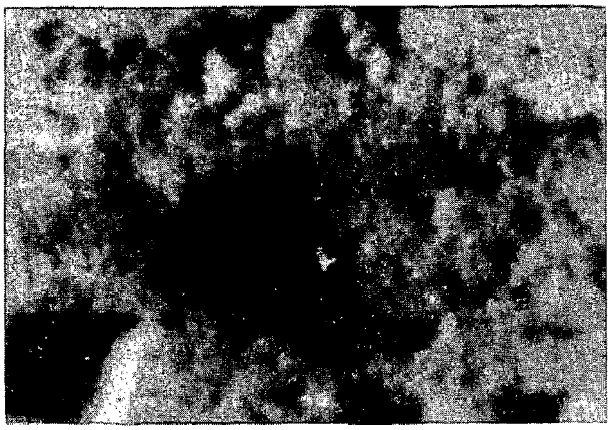

Figure 2. *Oil droplet on filter paper as seen under microscope magnification X100.*

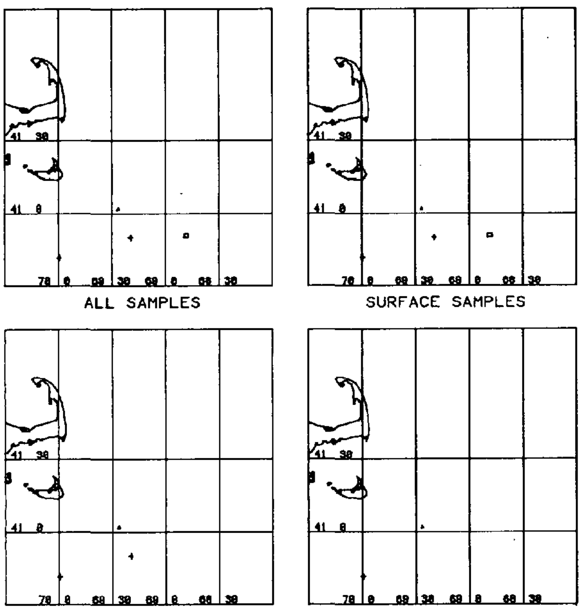

Figure 3. *Location of filters with (0) and without (+) oil droplets.*

filters for this cruise are summarized in Table 1. The locations of the various stations as a function of depth are indicated in Figure 3 where + indicates a sample with no oil and □ indicates a sample with at least one oil droplet. The location of the wrecked *Argo Merchant* is indicated by a △.

R/V Endeavor Cruise EN-003. The samples from this cruise showed no oil in a preliminary scan. The filters were considered to be too damaged to carry out a detailed analysis.

R/V Endeavor Cruise EN-004. A significant number of samples from this cruise were analyzed in detail and no indication of oil was found on any of the filters. Table 2 summarizes those analyzed and Figure 4 shows the sampling locations.

R/V Endeavor Cruise EN-005. Oil droplets exceeding 100 μ were detected at several locations from this cruise. These locations are shown in Figure 5. The location of the bow and stern sections of the *Argo Merchant* are marked in the figure with a △ and a "b" and an "s", respectively. The sizes of the □'s designating locations where oil droplets were found have been made proportional to the square of the number of droplets observed, this to give the reader a feeling for the density of droplets. There are several points worth stressing with regard to the analysis of the filters from this cruise (see Table 3).

1. Oil droplets were found at *all* three levels for which samples were taken: surface, mid-depth (generally below the surface 6m) and 1 meter above the bottom.
2. The oil droplets observed may be divided into three groups determined by their structure.
   a. Oil with no sediment in or adhering to the droplet.
   b. Oil droplet with sediment particles inside.
   c. Sediment coated with oil.
3. The droplets in the three classes listed above had a characteristic length in the 100 μ to 500 μ range.
4. The concentration of droplets (number of droplets per liter) is order-of-magnitude similar to that observed by Forrester; mean separation of 10cm to 20cm or about 1 droplet per liter.
5. The trail of oil droplets observed for this cruise, i.e. to the southwest from the wreck, is similar to that observed for oil in the bottom sediments (Hoffman and Quinn, 1978). Small oil droplets were observed to leave the sediment samples when stirred. One might conclude from this and the fact that some of the oil droplets contained sediment that the droplets observed in the filtered samples are being released from the sediments.

Table 1. Millipore Filter Results from R/V *Endeavor* Cruise EN—002

Station #	Depth Meters	Sampling Technique	Latitude/Longitude	Volume Sampled ML	#of Drops	Concentration* PPB	Oil in Sediments
1	1	Nisken	40°41.5′ 69°59.4′	850	0	0	---
1	6	Nisken	40°41.5′ 69°59.4′	1100	0	0	---
1	39	Nisken	40°41.5′ 69°59.4′	800	0	0	---
2	0	Bucket	40°50.1′ 69°19.4′	1000	0	0	---
2	6	Nisken	40°50.1′ 69°19.4′	1100	0	0	---
3	0	Bucket	40°51.0′ 68°48.3′	1500	1	3.1	No

*The concentration is that resulting from the oil droplets only.

Table 2. Millipore Filter Results from R/V *Endeavor* Cruise EN–004

Station	*Depth Meters*	*Sampling Technique*	*Latitude/Longitude*	*Volume Sampled ML*	*# of Drops*	*Concentration* PPB*	*Oil in Sediments*
A34	1	Nisken	41° 2.5' 69°17.5'	750	0		
A34	6	Nisken	41° 2.5' 69°17.5'	750	0		
A34	BOT	Nisken	41° 2.5' 69°17.5'	750	0		
G41	1	Nisken	41° 6.5' 69°22.3'	750	0		
G41	6	Nisken	41° 6.5' 69°22.3'	750	0		
G41	BOT	Nisken	41° 6.5' 69°22.3'	750	0		
G42	1	Nisken	40°54.8' 69°36.1'	750	0		
G42	6	Nisken	40°54.8' 69°36.1'	750	0		
G42	BOT	Nisken	40°54.8' 69°36.1'	750	0		
D36	1	Nisken	41° 0.9' 69°31.9'	750	0		
D36	BOT	Nisken	41° 0.9' 69°31.9'	750	0		
C39	1	Nisken	41° 3.3' 69°26.2'	750	0		
C39	6	Nisken	41° 3.3' 69°26.2'	750	0		
C39	BOT	Nisken	41° 3.3' 69°26.2'	750	0		
B15	1	Nisken	40°39.5' 68°22.0'	750	0		
B15	6	Nisken	40°39.5' 68°22.0'	750	0		
B11	1	Nisken	40°46.8' 68°22.0'	750	0		
B10	6	Nisken	40°51.6' 68°20.7'	750	0		
A40	6	Nisken	40°56.8' 69°31.5'	750	0		
A33	BOT	Nisken	41° 2.4' 69°13.9'	750	0		
E30	BOT	Nisken	40°50.2' 69°15.9'	750	0		

*The concentration is that resulting from the oil droplets only.

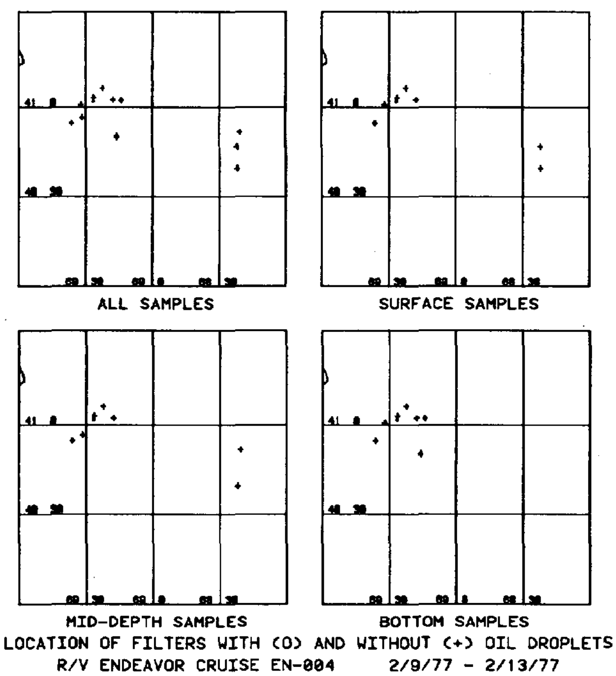

Figure 4. *Location of filters with (0) and without (+) oil droplets.*

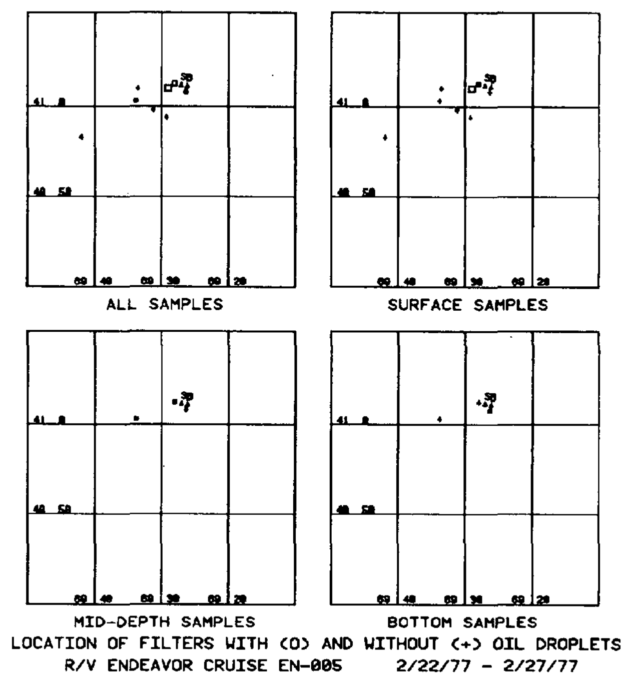

Figure 5. *Location of filters with (0) and without (+) oil droplets.*

Table 3. Millipore Filter Results from R/V *Endeavor* Cruise EN—005

Station	*Depth Meters*	*Sampling Technique*	*Latitude/Longitude*	*Volume Sampled ML*	*# of Drops*	*Concentration* PPB*	*Oil in Sediments*
48	0	Bucket	40°56.6' 69°41.9'	500	0	0	---
57	0	Bucket	41° 2.0' 69°33.5'	500	0	0	---
72	0	Bucket	40°58.8' 69°29.2'	500	0	0	---
74	0	Bucket	40°59.6' 69°31.2'	1000	0	0	---
59	1	Nisken .	41° 2.5' 69°28.0'	500	1	1.6	No
59	6	Nisken	41° 2.5' 69°28.0'	500	1	3.8	Yes
59	BOT	Nisken	41° 2.5' 69°28.0'	500	0	0	---
75	0	Bucket	41° 2.0' 69°29.0'	1000	0	0	---
70	0	Bucket	41° 1.6' 69°26.3'	1000	4	100.	No
70	1	Nisken	41° 1.6' 69°26.3'	500	0	0	---
70	6	Nisken	41° 1.6' 69°26.3'	500	0	0	---
70	38	Nisken	41° 1.6' 69°26.3'	500	1	?	Yes
58	1	Nisken	41° 0.6' 69°33.8'	500	0	0	---
58	6	Nisken	41° 0.6' 69°33.8'	500	1	4.5	Yes
58	BOT	Nisken	41° 0.6' 69°33.8'	500	0	0	---

*The concentration is that resulting from the oil droplets only.

Conclusions

None of the techniques now available are sufficiently sophisticated to detect small, <100 μ, oil droplets under conditions with high concentrations of suspended sediments in the water column and/or a large number of microorganisms. Furthermore, the volume of water sampled is too small to obtain useful results on the distribution of larger droplets, >100 μ.

It was possible, however, to obtain interesting results with regard to the structure of 100 μ and greater droplets specifically whether or not they contained sediments. Three general droplet structures were identified:
1. Pure oil with no sediments in or adhering to the droplet;
2. A large oil droplet, between 100 μ and 500 μ, with small particles of sediment inside; and,
3. A large piece of sediment, between 100 μ and 500 μ, coated with oil.

Those samples with droplets falling in class 1 were taken from the surface (bucket samples) or one meter below the surface (Nisken bottle). Those samples with droplets falling in classes 2 and 3 were taken at 6 meters and a meter above the bottom.

Unfortunately, very little is understood about the oil droplet-sediment interaction. More data of the type described above are required to determine if the trends observed here are real or not. If indeed they are real it may indicate that the droplets from different classes come from different sources. Specifically class 2 and 3 droplets may come from the sediments having been trapped there earlier while class 1 droplets may still have been leaking from the wreck.

Acknowledgments

Thanks go to Dave Konigsberg for constructing the apparatus and collecting the samples on EN-004, to Tatsusaburo Isaji for collecting the samples on EN-005, and to Sergio Antunes for analyzing part of the samples.

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Chemical Studies

James G. Quinn, Chairman

Summary of Chemical Studies

Chemical analysis of water samples indicated that physical or chemical fractionation of the *Argo Merchant* oil occurred with only the lighter hydrocarbons entering the water column. These components were probably associated with the cutter stock used in blending this particular oil.

Fluorescence spectroscopic analysis of water samples collected in late December, 1976 from the area surrounding the grounded vessel indicated concentrations of petroleum as high as 340 ppb. Subsequent analysis of samples from the same area collected in January and February, 1977, showed reduced levels of less than 20 ppb.

Water samples were also collected from the Georges Bank/Nantucket Shoals region and analyzed by gas chromatography and combined gas chromatography/mass spectrometry. Samples collected in February, 1977 showed concentrations varying from 10-100 ppb total hydrocarbons with a mean of 44 ppb. Concentrations fell off rapidly in May, 1-50 ppb ($\bar{X} = 11$ ppb), and levelled off thereafter to the 1-20 ppb range in August, 1977.

Tar balls found on the shores of Massachusetts and Rhode Island between two and three months after the spill were analyzed by infrared spectrometry. Based on these analyses, it was concluded that the *Argo Merchant* oil was not the source of these tar balls. There was some indication that they may have come from the lost tanker, *Grand Zenith.*

Thirty-seven samples of biota, collected from the vicinity of the spill area in December, 1976 and January, 1977, were analyzed by gas chromatography and combined gas chromatography/mass spectrometry. Three samples of fish stomach contents gave hydrocarbon distribution patterns which resembled the *Argo Merchant* oil.

Gas chromatographic analysis of sediment samples collected in February, 1977 indicated that three stations at the wreck site contained *Argo Merchant* oil in the form of small tar particles. In July, 1977, only one of these stations contained petroleum hydrocarbons and the level was greatly reduced over that found in February. The high degree of turbulent mixing on the shoals was probably responsible for the observed patchiness and removal of contaminated sediments.

In order to provide additional information on the *Argo Merchant* spill, the chemical studies workshop recommends the following:

1) Obtain samples of cargo oils from the refinery in Venezuela. These samples would be of use in chemical matching of samples collected from the spill area (e.g. biota samples analyzed by NOAA).

2) Collect and analyze water samples from the Nantucket Shoals-Georges Bank region during the winter of 1978. The February, 1977 values reported by Dr. Paul Boehm were high and additional winter samples are needed to determine if these values are due to the *Argo Merchant* spill or normal winter ship traffic in the area. (Data from the Mid-Atlantic region should be reviewed with this point in mind). The information obtained from additional analyses would be important in evaluating the effects of the *Argo Merchant* spill as well as providing background data on the Georges Bank region.

In order to provide an adequate response for future oil spills, the chemical studies workshop endorses the pending proposal to form an expanded spilled oil research team. This interagency team would consist of personnel from the EPA, FWS, NOAA and USCG, and be organized under the National Response Team. In our view, a coherent team effort appears to be the best approach to the study of fate and effects of oil spills including ecological damage assessment.

James G. Quinn, Chairman
Chemical Studies Session

Water Soluble Fraction of *Argo Merchant* Cargo

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Groton, Connecticut

The *Argo Merchant*, carrying 7.7 million gallons of blended Venezuelan No. 6 residual fuel oil (having a 2°C pour point and a 0.96 specific gravity) ran aground on the shoals of Nantucket Island, subsequently discharging the bulk of its cargo into the marine environment. A series of water column samples was collected in the area surrounding the wreck site shortly after the grounding to determine the extent and level of petroleum oil hydrocarbons entering the environment as a result of this pollution incident. Fluorescence spectroscopic analysis of these samples indicated that a physical/chemical fractionation of the oil occurred with only the lighter aromatic components (one-, two-, and three-membered ring aromatic compounds) entering the water column. These aromatic hydrocarbons are undoubtedly associated with the cutter stock material used in blending the industrial No. 6 fuel oil cargo carried by the *Argo Merchant*. Analysis of water column samples collected during the period of 20 through 28 December 1976 in the area surrounding the grounded *Argo Merchant* and along the direction of surface oil movement (to the southeast) indicated petroleum oil concentrations as high as 340 ppb. Subsequent analyses of water column samples collected throughout this area during January and February 1977 revealed that the relatively high petroleum levels found in December were reduced to levels less than 20 ppb.

Introduction

During the early morning hours of 15 December 1976, the *Argo Merchant*, carrying a cargo of 7.7. million gallons of an industrial No. 6 fuel oil, ran aground on the shoals of Nantucket Island. Attempts undertaken to off-load the cargo between 15 and 20 December were made impossible by gusting 40 knot winds and seas running up to twenty feet. Surveillance overflights during this period revealed a daily increase in the leakage of oil into the marine environment from the abandoned vessel. On the morning of 21 December 1976, the *Argo Merchant* cracked in half and discharged approximately one and a half million gallons of its cargo into the ocean. During the next few days practically all of the remaining cargo was discharged into the environment. Predictive models to describe the surface drift of oil as a function of the prevailing wind and surface currents were available and were used effectively to predict the surface movement of oil. However, models to predict the subsurface dispersion of oil do not exist, largely because the process of subsurface oil dispersion is relatively unknown at this time. In an effort to gain information on the subsurface dispersion of oil, a series of water column samples were collected by the U.S. Coast Guard, National Oceanic and Atmospheric Administration, Woods Hole Oceanographic Institute, and the University of Rhode Island during the period 20 December 1976 through 28 February 1977.

Collected water column samples were analyzed by synchronous excitation/emission fluorescence spectroscopic techniques. This method as previously described by Gordon et al. (1976) was selected as a rapid screening technique for handling large numbers of samples for three basic reasons: first, fluorescence spectroscopic techniques are quantitatively accurate when the type of spilled oil is known and is available for use as a calibration standard; second, the spectral fluorescence excitation/emission response of the polyaromatic compounds present in a sample is both readily distinguishable and indicative of the type of petroleum oil present; and third, fluorescence spectroscopic instrumentation is rugged and readily adaptable for shipboard use.

Experimental

Water column samples were collected using Niskin bottle, rosette or sterile bag samplers, and were either: (a) extracted and analyzed aboard ship using fluorescence excitation/emission spectroscopic techniques; or (b) immediately frozen and returned to the laboratory for analysis. Portions of the collected sample (100 ml or 1,000 ml) were extracted with spectroquality hexane. One liter volumes were extracted twice with two

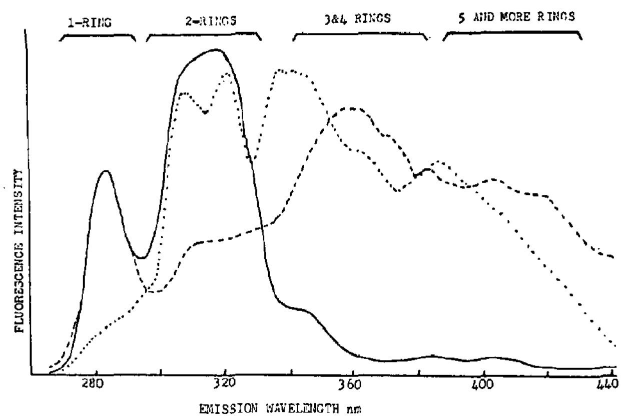

Figure 1. *Synchronous excitation/emission spectra of three oil types: No. 2 fuel oil (——); No. 6 fuel oil (. . . .); Bunker C (----).*

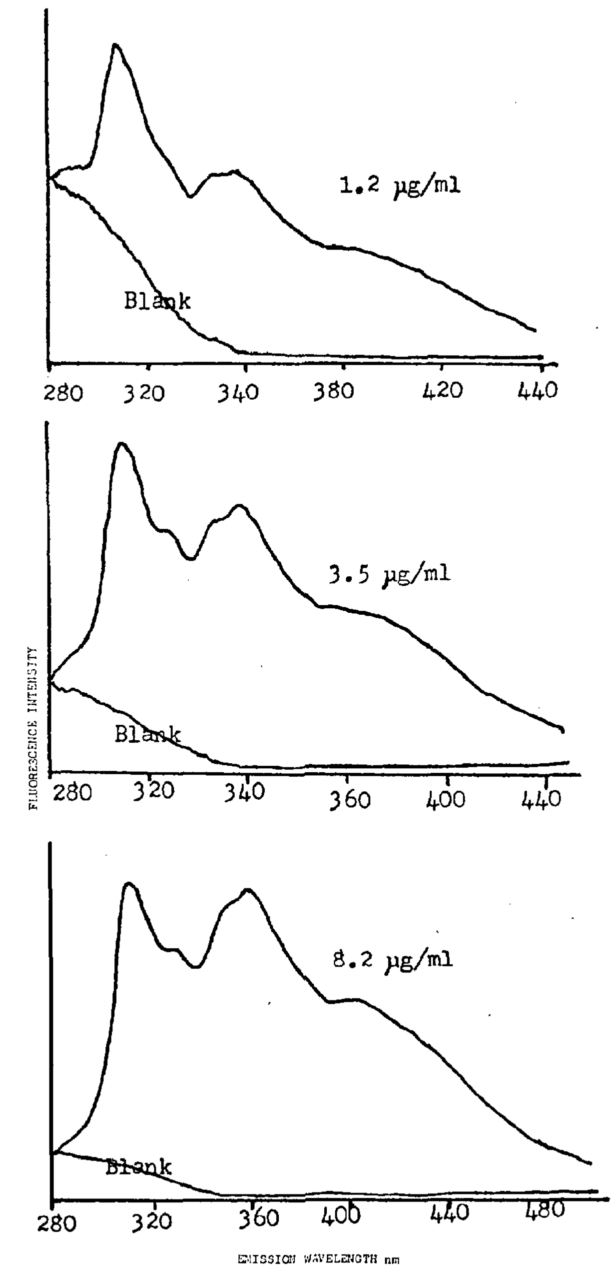

Figure 2. *Synchronous excitation/emission spectra of Argo Merchant cargo at three concentrations.*

10 ml aliquots of hexane, whereas 100 ml volumes were extracted once with 10 ml of hexane. All extractions were performed in a separatory funnel by hand shaking the hexane/sea water mixture vigorously for two minutes.

All fluorescence excitation/emission analyses were performed using a fully corrected Farrand Mark I Spectrofluorometer. All spectra were recorded using an excitation bandpass of 10 nm; an emission bandpass of 2.5 nm; and a scan speed of either 30 or 50 nm/minute, with a constant offset of 25 nm between the excitation and emission monochromators.

Discussion

Fluorescence spectroscopy, and in particular fluorescence synchronous excitation/emission techniques, have been used to qualitatively characterize and identify the presence of petroleum oils based on the distribution of polyaromatic hydrocarbons (Gordon et al., 1976; Lloyd, 1971a; Gordon and Keiser, 1975). The synchronous excitation/emission spectra of several oil types are shown in Figure 1. As can be seen from Figure 1, the various oil types can be characterized based on the distribution of the one-, two-, and multiple-ring compounds. Benzene type compounds emit strongly in the 280 to 290 nm region, napthalenes between 310 to 330 nm region, three and four membered ring compounds between 340 and 380 nm, and larger ring compounds above 400 nm. Additionally, it has been shown that between the concentration range from 1 μg/ml to 100 μg/ml the strong fluorescence emission from both low and high molecular weight aromatic components insures a highly structured spectral profile (John and Soutar, 1976). Figure 2 shows the synchronous excitation/emission spectra of *Argo Merchant* oil at several concentration levels. As can be seen from Figure 1, the *Argo Merchant* oil has a spectrum similar to that of a No. 6 fuel oil, containing a wide distribution of polyaromatic compounds.

Figure 3 shows a typical fluorescence excitation/emission profile obtained in the analyses of sea water samples collected in December 1976 from the area surrounding the wreck site of the *Argo Merchant* which is distinctly different from the spectral profiles of *Argo Merchant* oil shown in Figure 2. The majority of samples collected in this investigation were obtained using Niskin sterile bag samplers. Gordon and Keizer (1974) have shown that the sampling device presents a problem in the fluorescence analysis of sea water samples, mainly through desorption and adsorption processes taking place between the collected sample and the walls of the sampling device. Figure 4 shows three spectral profiles of sea water which had been in contact with sterile bag samplers for various periods of time, 1 hour, 2 weeks and one month at room temperature. Except for an increase in the response in the 300 to 304 nm region of the spectral profile the spectral response shows the absence of two or more ring aromatic compounds. Additionally, Figure 5 shows the hexane extract of the sterile bag used in

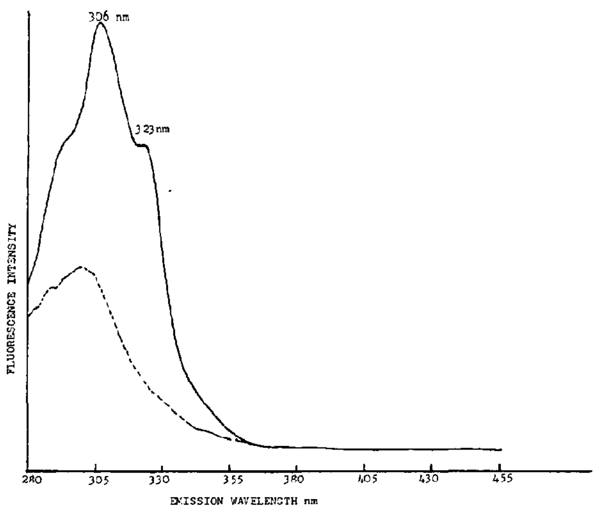

Figure 3. *Synchronous excitation/emission spectra of sea water sample collected in December 1976 (——); and sea water blank (----).*

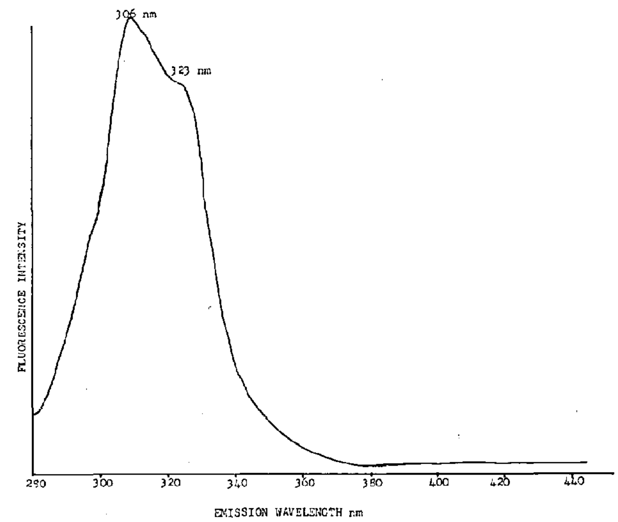

Figure 5. *Synchronous excitation/emission spectrum of the hexane extracted sterile bag containing the sea water sample shown in Figure 3.*

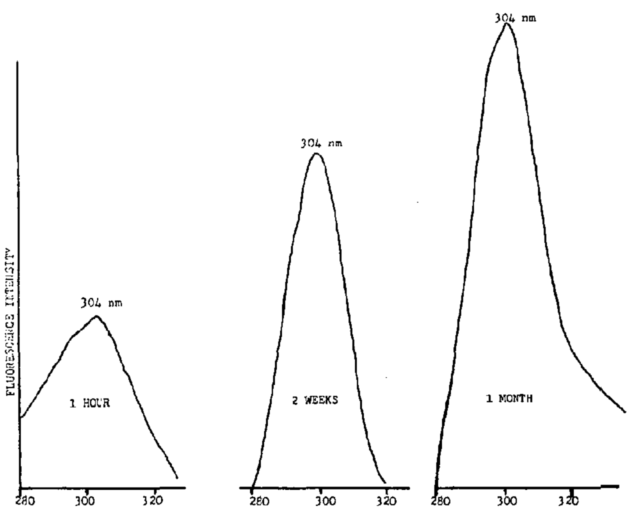

Figure 4. *Synchronous excitation/emission spectra of sea water after storage in a sterile bag at room temperature for an extended period of time.*

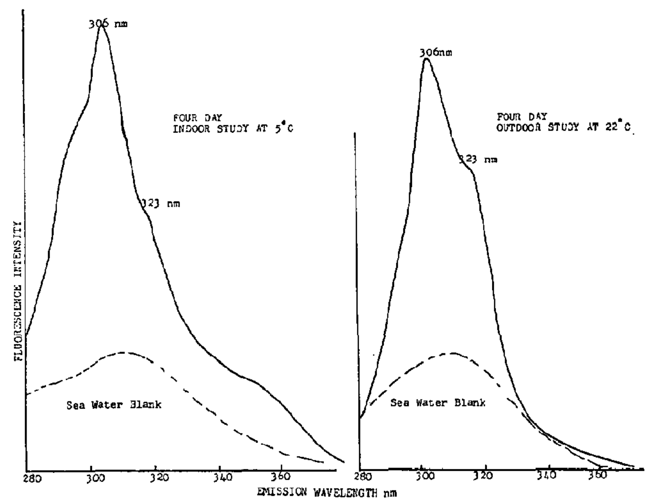

Figure 6. *Synchronous excitation/emission spectra of sea water after exposure to Argo Merchant oil for a four day period.*

collecting the sample shown in Figure 3. Although the walls of the bag have apparently absorbed some of the aromatic hydrocarbons present, there is no evidence of higher molecular weight hydrocarbons having been absorbed. Figures 4 and 5 illustrate that although the sterile bag samplers do offer a source of contamination in fluorescence analyses, and absorb aromatic hydrocarbons, neither the fluorescent contaminant induced from the bag, nor use of the sterile bag itself, can explain the spectral response obtained in the analyses of the typical sea water sample shown in Figure 3. Furthermore, the effect of this contaminant can be minimized if the samples are processed immediately after collection as shown in Figure 4 (one hour). This was evident in the shipboard analysis of samples collected on the January 1977 R/V *Endeavor* cruise, where samples collected using Niskin bottle or sterile bag samplers had identical spectral responses.

In an effort to explain the repeated occurrence of the spectral profile shown in Figure 3, two separate laboratory studies were undertaken. These two laboratory studies involved the gentle spreading of *Argo Merchant* oil on sea water and allowing it to stand for a four day period. The sea water used in this study was a composite of samples collected on board the R/V *Oceanus* 19 cruise, prior to the break-up of the *Argo Merchant*. Figure 6 shows the synchronous excitation/emission profiles of extracted subsurface water samples from both studies. There does exist a slight difference in the spectral response of the 5°C indoor, compared with the average

22°C outdoor, test, but in each study there is a complete absence of high molecular weight aromatics. These differences can be explained by the relative solubility of aromatic hydrocarbons in water (Bohon and Claussen, 1951; Boylan and Tripp, 1971) and the effects of weathering on the change in the synchronous excitation/emission profile of subsurface water samples taken from beneath an oil slick (Gordon et al., 1976). Additionally it was shown in the weathering of a Guanipa crude oil in an outdoor test tank that the proportion of two tinged aromatics in samples taken 0.5 meters beneath the surface increased relative to the higher molecular weight aromatics during the course of this study. However, the spectral profiles shown in Figure 6, for the study conducted at 5°, remained unchanged over a four day period. The only difference observed in samples taken at 24 hour intervals was an increase in the relative intensity of the spectral response, with no evidence of higher weight aromatics being present.

The spectral responses shown in Figure 6 are similar to that shown in Figure 3, apparently indicating that some type of fractionation of the *Argo Merchant* oil occurred. Studies by Anderson et al. (1974) showed that when oil is spilled or discharged into the environment two distinct oil-water fractions are formed: a water-soluble oil fraction (WSF) and an oil-water dispersion (OWD). The magnitude of each fraction occurring after a discharge is dependent on the type and amount of oil discharged; the rate and type of discharge (slow leak, pumping, rupturing of tanks, etc.); and the existing environmental conditions. In high sea states the OWD fraction will be significant, with its extent being dependent on the physical characteristics of the oil in question, i.e. its pour point, API gravity, etc. These same physical parameters will also affect the spreading characteristics of oil on water, the magnitude of oil-in-water emulsions being formed and the speed at which the oil will undergo weathering changes (solution, evaporation, bio-degradation, etc.).

At the time of the grounding, the *Argo Merchant* was carrying a blended Venezuelan No. 6 residual fuel oil cargo having a specific gravity of 0.96 and a pour point of 2°C. When this cargo was discharged into the environment, large "pancakes" were formed 1½ to 2 inches thick and were reported to behave "like mercury" (Milgram, 1977). Overflights revealed oil sheens generally upwind of the pancakes. The viscous nature of this spilled oil resulting from both the oil's pour point and existing water and air temperatures, 5° to 6°C, prevented any rapid spreading of oil on water. This also reduced the amount of oil which could be mechanically driven into the water column to form the OWD fraction.

Anderson et al. (1974) studied the behavior of 4 API reference oils (Kuwait and South Louisiana crude oils, and No. 2 and Bunker C fuel oils) in sea water. They observed that the WSF fractions of the four test oils were greatly enriched in the aromatic hydrocarbons (one-, two- and three-membered aromatic ring compounds) in comparison to the parent oil, whereas the OWD fractions contained a distribution of hydrocarbons resembling that of the parent oil. Similar results have also been reported in the analysis of water which had been in contact with other oil types (Boylan and Tripp, 1971). The water soluble components in these studies were again benzene and naphthalene type compounds. Additionally these studies indicated that oil-in-water emulsion contained a distribution of hydrocarbons similar to that of the parent oil used in these studies.

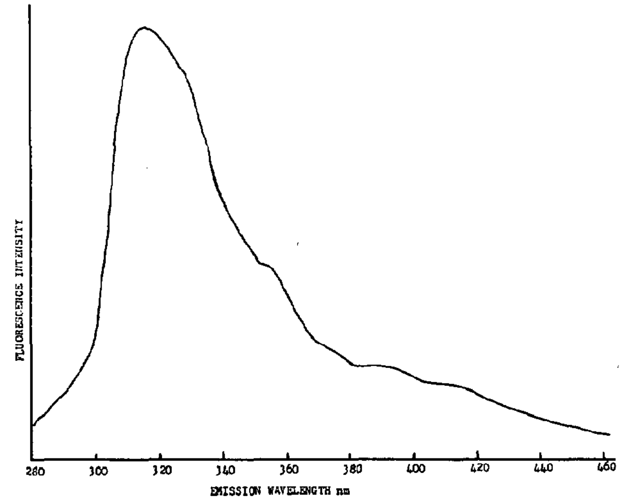

Figure 7. *Fluorescence emission spectrum of the extracted sea water sample shown in Figure 3; excitation wavelength 254 nm.*

Studies by Milgram (1977) revealed that the *Argo Merchant* cargo contained 20 percent of a light petroleum fraction. This fraction is believed to be a "cutting stock" distillate used to blend with the residual fuel oil to improve the oil's handling characteristics in obtaining the observed 2°C pour point of the cargo. Furthermore, Milgram found that after removing the light petroleum fraction by distillation the specific gravity of the residual fuel oil remained unchanged: 0.96. The cargo carried by the *Argo Merchant* was similar in composition to that carried by the tanker *Arrow* which went aground in Chedabucto Bay, Nova Scotia, during 1970. Both cargos were blended Venezuelan residual fuel oils. Studies by Mackay et al. (1973) and Betancourt and McLean (1973) showed that weathering processes (evaporation, biodegradation, solution) affects the composition of the spilled oils by removing the light aromatics and increasing the asphaltene concentration which is associated with a large increase in the viscosity of the oil phase preventing both the coalescence and sedimentation of the water-in-oil emulsion droplets. This was observed to be particularly true for residual fuel oils spilled in cold water.

Results

Recent studies (Cretney et al., 1977) have suggested the use of any aromatic standard, chrysene, as a standard which could be used to report sea water petroleum oil concentrations. Chrysene was selected because the fluorescence excitation/emission response of chrysene was found to be similar to that of a heavy fuel oil. Others (Hiltebrand, in press; Levy, 1973) have selected the maximum fluorescence emission band of the parent oil, when excited at a fixed wavelength, to establish a calibration curve to determine sea water petroleum oil concentrations. In this study the selection of either approach would have yielded misleading values. Figure 7 shows the fluorescence emission curve of the extracted sea water sample shown in Figure 3 when excited at a fixed wavelength of 254 nm. There exists no significant response in the 365 nm region, the major fluorescencing region, when a fixed wavelength of 254 nm is used, or the 366 nm, 383 nm and 400 nm region if

Table 1. Estimated Petroleum Concentration Levels (ppb) During December 1976

Latitude (N)	*41°07.0′*	*40°52.0′*	*40°45.0′*	*40°55.0′*
Longitude (W)	*69°56.0′*	*69°35.0′*	*68°25.0′*	*67°56.0′*
Surface	230	250	0	310
5 Meters	310	150	180	140
10 Meters	—	200	270	—
20 Meters	—	210	170	—
Latitude (N)	*41°01.3′*	*41°01.4′*	*40°58.5′*	*41°03.0′*
Longitude (W)	*69°22.0′*	*69°26.1′*	*69°24.0′*	*69°34.0′*
Surface	120	90	170	40
3 Meters	0	0	0	120
Latitude (N)	*41°00.0′*	*41°01.6′*		*40°48.8′*
Longitude (W)	*69°25.5′*	*69°28.6′*		*69°04.0′*
Surface	—	270	79 Meters	170
3 Meters	340	—		

chrysene were used as a standard. If either of these two methods were employed to report sea water petroleum oil concentrations in the area surrounding the *Argo Merchant* wreck site immediately after its break-up, negligible concentrations would have been reported.

Table I lists "estimated" petroleum oil concentrations for representative samples collected during the period 22 through 24 December 1976. All reported concentrations are relative to the cargo carried by the *Argo Merchant.* Figure 2 indicates two fluorescencing bands, one at 306 nm, and the second at 323 nm. The ratio of these two band intensities were plotted against concentration. These same two bands are seen in Figure 3, a typical synchronous excitation/emission spectrum of an extracted sea water sample. Those samples showing zero petroleum oil concentrations in Table I were used as blanks in calculating the other sample concentrations listed in Table I. The synchronous excitation/emission spectra of these samples selected as blanks had no significant spectral features in the 306 nm or 323 nm region. Additionally, these samples had the same residence time in the sterile bags, minimizing any possible effects of absorption processes which may have occurred in storage of these samples between collection and analysis times.

Conclusions

The fluorescence emission spectrum of the sample shown in Figure 7 is typical of that which would be obtained if the sample in question was a No. 2, or light distillate fuel oil. The samples listed in Table I all have the same spectral response indicating the presence of a No. 2, or light distillate fuel oil. Previous investigators have shown the rapid solubility of light aromatic compounds in sea water, and regardless of the parent oil used in these studies, the same water soluble components were found to be present. These one-, two-, and three-membered ring aromatic compounds are commonly associated with light distillate fuel oils. The high percentage of "cutting stock" material used in blending the residual fuel oil carried by the *Argo Merchant* is undoubtedly responsible for the petroleum level concentrations reported in Table I. Since a sample of this cutting stock material was not available, the concentrations listed in Table I are estimates based on the response of the *Argo Merchant* oil in the 306 nm and 323 nm region.

Analysis of samples collected in January and February 1977 from the area surrounding the wreck site indicated that the high levels found in December 1976 had dissipated. Synchronous excitation/emission spectra of these samples were similar to those obtained from samples collected on the R/V *Oceanus* 19 cruise prior to the break-up of the *Argo Merchant.*

This study has demonstrated that the use of fluorescence spectroscopic techniques to quantify petroleum oil concentration levels is strongly dependent on the selection of a standard. Prior to selecting a standard, whether it be the parent oil or a single aromatic compound or mixtures of aromatics, it is advisable to analyze the collected samples by synchronous excitation/emission techniques to determine the distribution of aromatic compounds present. If only a mixture of one-, two-, and three-membered ring compounds is present, and an oil-in-water dispersion is not obvious, then a mixture of one-, two-, and three-membered ring compounds should be selected as a standard. Based on the work of previous investigators, this would be a logical choice for a standard, since the water soluble compounds which are shown to be readily soluble are light aromatics, regardless of the parent oil. Furthermore, the use of standards which have responses similar to heavy oils or relying on the major fluorescencing band of heavy oils to determine petroleum oil concentrations can lead to erroneous results, particularly if a physical/chemical fractionation of the oil has occurred, as is suspected in the analyses of water samples collected after the *Argo Merchant* oil spill.

The opinions or assertions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Commandment or the Coast Guard at large.

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Hydrocarbon Chemistry of the Water Column of Georges Bank and Nantucket Shoals, February–November 1977

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Abstract

Large volume water samples (50-90 liters) were collected in mid-February, May, August and November of 1977 at twelve stations in the Georges Bank/Nantucket Shoals region. Near surface and bottom samples were filtered on-board and the filtrate extracted in the laboratory, using a countercurrent liquid-liquid extractor. Aliphatic and aromatic hydrocarbon compositions of the particulate and dissolved fractions were determined by glass-capillary gas chromatography and combined gas chromatography/mass spectrometry.

Samples collected in the winter show markedly higher dissolved hydrocarbon concentrations than those analyzed from later seasons. Concentrations throughout the study area ranged from 10-100 ppb total hydrocarbons in the winter with a mean of 44 ppb. Concentrations fell off rapidly at the time of the spring cruise, 1-50 ppb ($\bar{x}$ = 11 ppb) and levelled off thereafter to the 1-20 ppb range. The entire study area showed elevated hydrocarbon levels at the time of the winter sampling.

Qualitatively the dissolved hydrocarbon assemblages in the winter appear to be a composite of: 1) lower boiling aliphatic and aromatic compounds (boiling range n-C_{14}-n-C_{22}); and 2) a higher boiling unresolved complex mixture (UCM). The lower boiling compounds are similar to those determined in a laboratory sea water accommodated fraction of *Argo Merchant* cargo oil. As the concentrations decreased throughout the year so did the relative contribution of these lower boiling compounds.

The hydrocarbon distributions in the particulate fraction varied from a direct coincidence with the dissolved fraction's distribution to ones more suggestive of biogenic inputs combined with pelagic tar.

Introduction

Four seasonal sampling cruises were undertaken during 1977 to characterize the benthic and water column hydrography, biology, and chemistry of the Georges Bank/Nantucket Shoals/Lower Gulf of Maine region. As part of the overall hydrocarbon chemistry program, large-volume water and surface microlayer samples were obtained to describe the dissolved and particulate hydrocarbon compositions of the region as they varied seasonally.

Virtually nothing was known of the detailed water column hydrocarbon chemistry of the region prior to this set of cruises. In fact, there is only limited information on the distribution of hydrocarbons in the water column of the world's continental shelves. A summary of some of the available hydrocarbon data is presented in Table I. A wide range of hydrocarbon concentrations has been reported. In some cases the lack of a consistent reporting format somewhat impairs our ability to intercompare values, but, in general, water column hydrocarbon concentrations have been reported in the 0.2 to 100 ppb concentration range. The higher values are found in areas of heavy shipping traffic.

Our study commenced six weeks after the breakup of the *Argo Merchant* oil tanker and in effect represents the only follow-up study undertaken which covers the entire region of Georges Bank and Nantucket Shoals. We present here a general overview of the data on the hydrocarbon distributions in the water column and the changes that took place in these distributions in the eleven months after the spill.

Methods

Sampling. Large-volume water samples (45-90 liters) were obtained at twelve stations shown in Figure 1. An anodized aluminum 90-liter Bodman bottle (Benthos Corp.) was deployed at the near surface (3 meters) and near bottom (3 meters off bottom) at each station. The design and operation of this sampler permits the bottle to be opened after it has passed through the potentially contaminating sea surface film. It is then lowered to

Table 1. Hydrocarbons in Sea Water

Location	*Concentration (μg/l)*	*Comments*	*Reference*
Georges Bank Region	0.2-98	Gas Chromatography (GC)	This study
South Texas OCS	0.1-2.0	Paraffins only	Berryhill (1977)
Alaska OCS		GC	Shaw (1977)
Gulf of Mexico Loop Current	0-75	GC	Iliffe & Calder (1974)
West African Coast	10-95	GC	Barbier et al. (1973)
French Coast	46-137	GC	Barbier et al. (1973)
Open Ocean (Atlantic)	1-50	IR	Brown et al. (1973)
	<6	Fluorescence	Gordon et al. (1974)
	20	1-3 mm Fluorescence	Gordon et al. (1974)
Mediterranean Sea	2-200	Surface (IR)	Brown et al. (1975)
	2- 8	Subsurface (IR)	Brown et al. (1975)
Atlantic	0.5-6		Brown et al. (1975)
Baltic Sea	50-60	Non-aromatics	Zsolnay (1972)
Gulf of Mexico (coastal)	.1-.6	*n*-alkanes only	Parker et al. (1972)
Galveston Bay area	8		Brown et al. (1973)
New York Bight	1-21		Brown et al. (1973)
Gulf of Venezuela	50		Brown et al. (1973)
Bedford Basin, Nova Scotia	1-60		Keizer & Gordon (1973)
Gulf of St. Lawrence	1-15		Levy & Walton (1973)
Narragansett Bay	8.5	GC	Duce et al. (1972)
	5-15	GC	Boehm (1977)
Woods Hole Harbor	11	GC	Stegemann & Teal (1973)

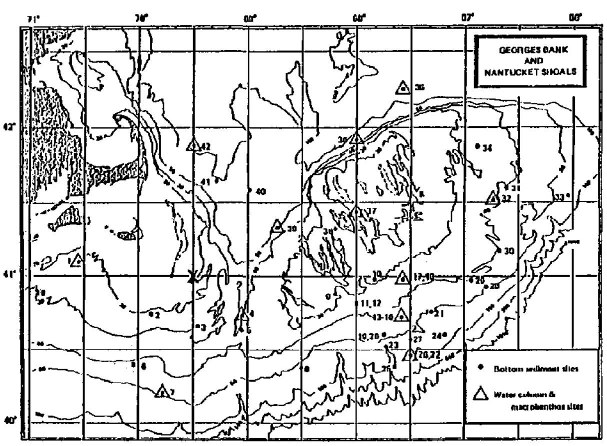

Figure 1. *Station locations and coordinates.*

depth, closed by messenger and brought aboard. Ninety liters are then pressure-filtered (10 psig) within one hour after sampling through a 142-mm pre-combusted Gelman A-E glass fiber filter set in a stainless steel filter holder. Water samples were collected in solvent-rinsed stainless steel drums (30-gallon) or 12-gallon glass carboys.

Surface microlayer samples were collected (7 liters = 60 m^2 of surface) at three stations in the winter, eight in the spring and seven in the summer, using the screen technique of Garrett (1965). Both the microlayer and dissolved samples were poisoned with chloroform on board to retard microbial degradation.

The samples were obtained on R/V *Gyre* cruises in the winter (February) and spring (May), aboard the R/V *Gillis* in the summer (August), and aboard the R/V *Knorr* in the fall (November).

Analytical Methods. Dissolved hydrocarbon samples were extracted in an all stainless steel and glass counter-current liquid-liquid extractor designed by A. Himmelblau of Energy Resources Co. Two and one-half liters of chloroform (Baker Resi - Analyzed) were used and 95 percent extraction efficiency achieved in four hours. This was determined by three successive extractions of a single sample of two hours' duration each.

The filters were thawed, placed in a round-bottom flask, and extracted with chloroform and hexane under reflux for four hours.

The surface microlayer samples were extracted in three-batch chloroform extractions in separatory funnels.

All of the extracts were reduced in volume on a rotary flash evaporator and concentrated to near dryness under a stream of water-pumped purified nitrogen. The total extractable lipid weight was determined by weighing an aliquot on a Cahn electrobalance. The total extract was then charged to a glass column (1 cm diameter) packed with 2.5 g 5% deactivated alumina over 7.5 g fully activated (200°C, 4 hours) 100-200 mesh silica (W.R.Grace Co.). The column was eluted with 18 ml hexane (fraction 1) followed by 20 ml benzene (fraction 2) to collect the aliphatic (f_1) and aromatic/olefinic (f_2) hydrocarbons. Concentration of these fractions by rotary evaporation was followed by their analysis by gas chromatography (GC). A Hewlett-Packard model 5840A gas chromatograph equipped with the HP 18835A glass capillary inlet system was used. The capillary column was a 15 meter (~50,000 theoretical plates) SE-30 column (J & W Scientific) and the samples run in the splitless mode.

Table 2. Dissolved Hydrocarbon Data Summary

Station No.	Depth	Total Hydrocarbon (µg/l) Winter	Spring	Summer
1	3	23.7	5.0	0.9
4	32	27.8	17.9	1.0
4	3	20.8	4.8	0.2
	64	16.3	5.8	–
7	3	48.9	2.8	–
	85	98.5	4.7	–
13	3	59.8	7.8	–
	80	10.2	1.8	3.1
18	3	27.4	9.0	0.3
	65	38.9	5.7	0.2
26	3	16.4	12.5	2.0/1.0
	150	19.7	1.2	1.5
32	3	22.6	17.4	0.8
	65	36.5	8.6	0.4
35	3	–	5.7	–
	230	–	4.5	–
36	3	–	49.0	0.2
	100	30.9	36.8	0.2
37	3	–	5.0	0.2
	30	–	10.7	0.8
39	3	32.5	20.4	0.3
	85	26.9	14.9	8.1
42	3	14.4	7.7	2.9
	190	47.5	7.3	1.3

Concentrations of hydrocarbons were determined by combining information on individual component concentrations, obtained from a PDP-10 computer interfaced to the GC through the HP 18846A Digital Communications interface. The unresolved complex mixture (UCM) was measured from the chromatograms directly by planimetry and quantified relative to the area of the internal standard.

Combined gas chromatography/mass spectrometry was performed on a Hewlett-Packard model 5981A quadrupole mass spectrometer coupled to a model 5710 gas chromatograph.

Results and Discussion

Dissolved Hydrocarbons. Total hydrocarbon concentrations in the "dissolved" fraction ranged from 10-100 ppb in the winter samples (Table 2). The average surface water (3 meter) concentration, 29.9 µg/ℓ, is not significantly different from the bottom water samples, 35.0 µg/ℓ. However, differences do appear when considering individual station concentrations. Table 2 indicates that the bottom waters at Stations 7 and 42 appear

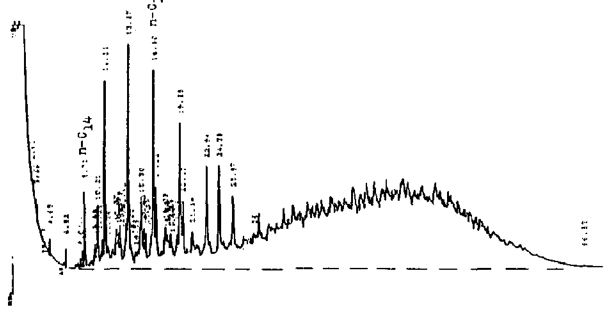

Figure 2A. *Dissolved hydrocarbons: winter, fraction1.*

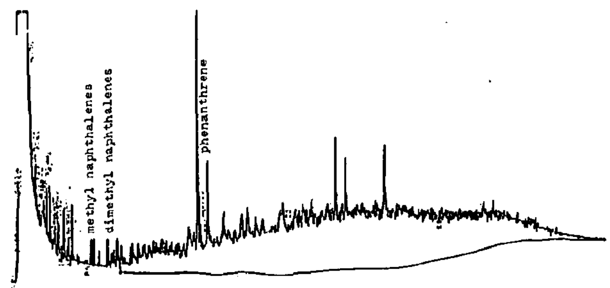

Figure 2B. *Dissolved hydrocarbons: winter, fraction 2.*

enriched in hydrocarbons relative to the surface waters while the surface waters at Station 13 are more concentrated than the near-bottom sample. At all other stations the water column appears well mixed in the winter, an observation consistent with the hydrographic data (Strimaitis, personal communication).

Information on sampling replication is not yet available. Duplicate subsamples of 45 liters each were analyzed on a split summer sample and results indicate a precision of ± 59 percent for an absolute sample concentration in the 1-2 µg/ℓ range.

At most of the stations, the total hydrocarbon concentrations decreased over the course of three seasons. At Stations 36 and 39 (surface and bottom) and at Stations 26 and 32 (surface), the winter and spring values remained constant, but then decreased with all of the other station concentrations in the summer (August 1977). Of special interest is the Station 26 data. The water column chemistry at this station is greatly influenced by an oceanographic frontal system alternately transgressing and regressing over the southern edge of Georges Bank (L. Sick, D. Strimaitis, personal communications). This frontal system became well developed at the time of sampling in the spring. The order of magnitude differences in the surface and near-bottom "dissolved" hydrocarbon values attest to our sampling of two different water masses at this station in the Georges Bank surface water and the deeper slope water.

"Dissolved" hydrocarbon concentrations in the spring (May) averaged 13.2 µg/ℓ (range 2.8-49.0) in the surface waters and 9.0 µg/ℓ (range 1.2-36.8) in the near-bottom samples. A further sharp decrease was noted in the summer samples, at which time surface waters averaged 0.8 µg/ℓ (range 0.2-3.1) and bottom waters 1.7 µg/ℓ

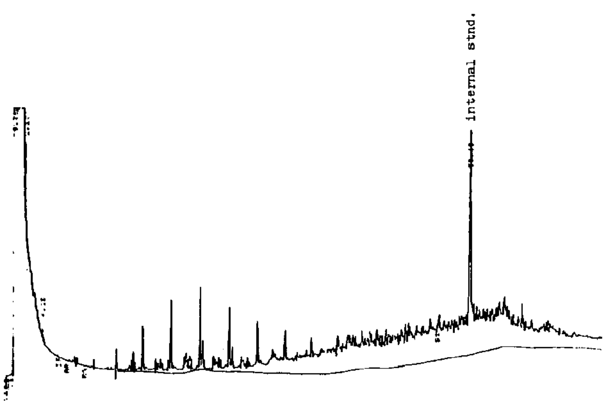

Figure 3A. *Dissolved hydrocarbons: spring, fraction 1.*

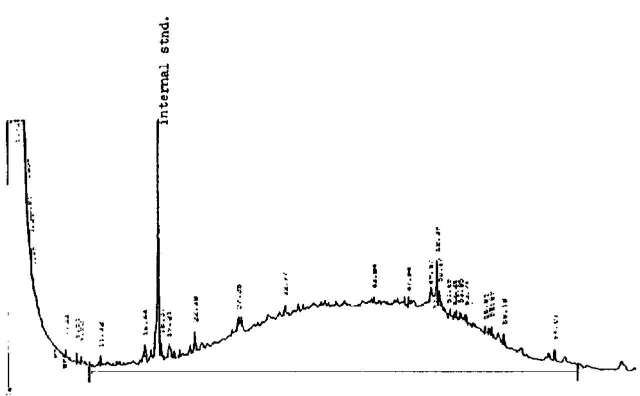

Figure 3B. *Dissolved hydrocarbons: spring, fraction 2.*

(range 0.2-8.1). Preliminary information on the fall (November) samples indicate that their concentration range is similar to the summer samples.

Analytical blanks were run periodically and all samples were at least twice the blank level (0.1-0.2 ppb). Values in Table 2 have been corrected for the blanks. In addition, shipboard samples of all fuel and lubricating oils were collected and chromatographed. Comparisons of the gas chromatograms of the oil samples and the water samples indicated that no shipboard contamination of the samples occurred.

More revealing than the total concentration data are the gas chromatographic characteristics of the samples. The f_1 (hexane eluate) chromatograms from the winter samples appear to be a composite of *n*-alkanes and branched alkanes in the *n*-C_{12}-*n*-C_{22} range, the typical boiling range of a No. 2 fuel oil, and an unresolved complex mixture (UCM) of coeluting hydrocarbons with a maximum detector response at *n*-C_{28} (Figure 2A). A chromatographic distribution similar to that found in this study has been observed by other researchers in the Gulf of Mexico Loop Current (Iliffe and Calder, 1974), and in the oil tanker route off the coast of Africa (Barbier et al., 1973).

The UCM generally accounts for 60 to 80 percent of the total determined hydrocarbon concentrations. This f_1 pattern was quite characteristic of the winter and spring samples, although present in lesser concentrations in the

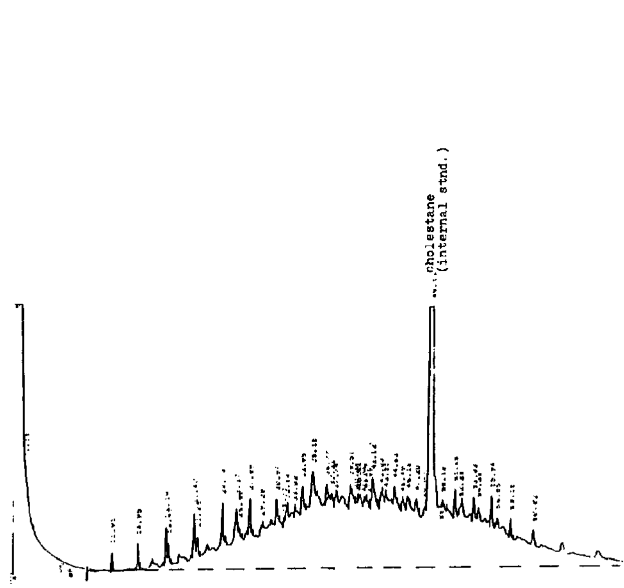

Figure 4A. *Dissolved hydrocarbons: summer, fraction 1 (2ppb).*

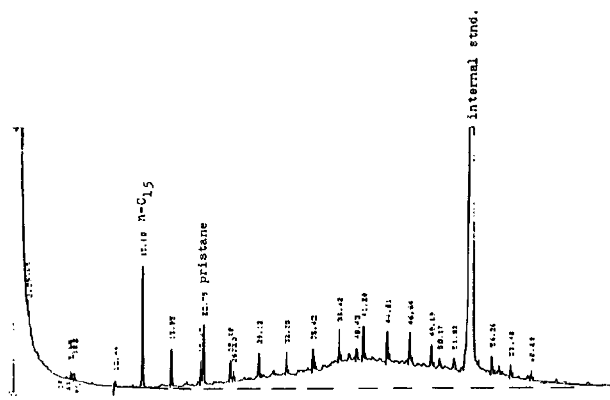

Figure 4B. *Dissolved hydrocarbons: summer, fraction 1 (2ppb).*

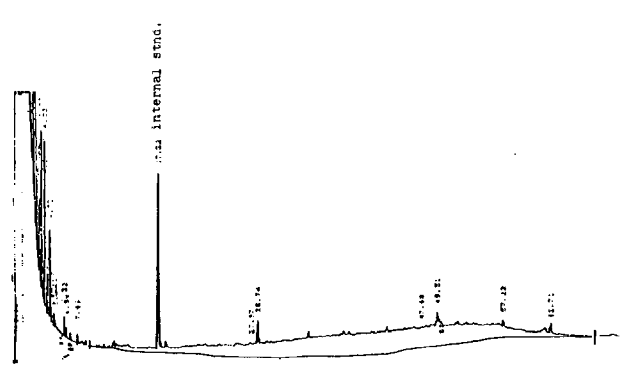

Figure 4C. *Dissolved hydrocarbons: summer, fraction 2.*

spring. The relative input of the *n*-C_{12}-*n*-C_{22} alkanes began to decrease in the spring samples (Figure 3A) and its predominance waned as the absolute concentrations decreased to the 0.2-2.0 ppb range found in the summer samples (Figure 4A and B). The f_1 hydrocarbon assemblage in the low-level (~0.5-2 ppb) summer dissolved samples revealed a relatively smooth *n*-alkane distribution from *n*-C_{16} through *n*-C_{31} with biogenic inputs of *n*-C_{15} and the isoprenoid pristane rising out of the chromatographic pattern (Figure 4B). This summer pattern is similar

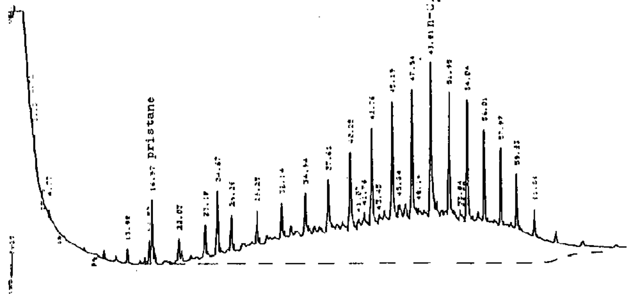

Figure 5A. *Surface microlayer: winter, fraction 1.*

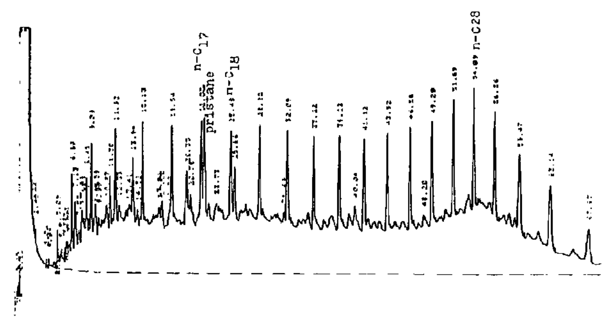

Figure 6A. *Argo Merchant cargo oil, fraction 1.*

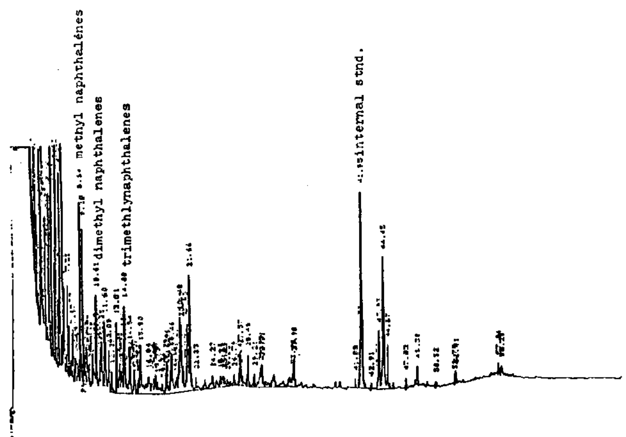

Figure 5B. *Surface microlayer: winter, fraction 2.*

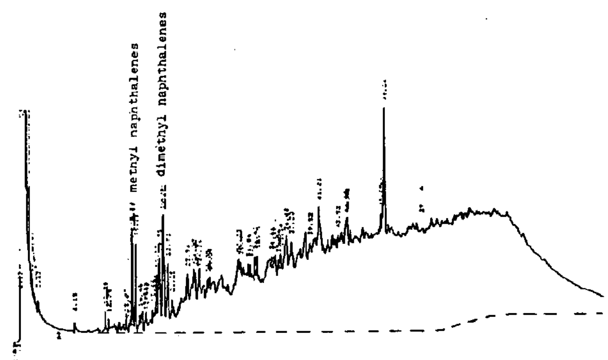

Figure 6B. *Argo Merchant cargo oil, fraction 2.*

to the surface microlayer samples obtained using the stainless-steel screening technique of Garrett (1965). However, in the case of the microlayer samples, the *n*-alkanes smaller than n-C_{25} appear depleted, relative to the dissolved samples (Figure 5A vs. Figure 4B).

The fraction 2 (benzene eluate) hydrocarbons of the winter (Figure 2B) and spring dissolved samples contain prominent methylated naphthalene components and phenanthrene and alkyl phenanthrene compounds (0.02-0.05 ppb). This distribution suggests a petroleum source. Likewise the surface film winter samples (Figure 5B) exhibit significant (0.05-0.1 μ g/ℓ) amounts of the naphthalene and phenanthrene series. Many samples also contain small amounts of fluoranthene and pyrene (m/e 202) compositions as determined by combined gas chromatography/mass spectrometry. Figure 2B is typical of a winter f_2 distribution in those samples of intermediate hydrocarbon concentrations (10-20 ppb). In this sample type, many aromatic hydrocarbons ride atop a broad UCM, an aromatic distribution closely resembling the *Argo Merchant* f_2 distribution (Figures 6B and 7). In the spring samples, the f_2 UCM dominates and resolved aromatic components are less frequently observed (Figure 3B). The summer samples, when containing total hydrocarbon concentrations of >1.0 μg/ℓ, exhibit an UCM along with a series of high molecular weight biogenic olefins (Figure 4C). As pristane achieved a chromatographic prominence in the summer f_1 samples, so did these olefins. A planktonic input is indicated.

Surface Microlayer. Along with the "dissolved" hydrocarbon samples, the surface microlayer samples exhibited lower hydrocarbon concentrations in the spring and summer than they did in the winter, averaging 54 μg/ℓ (range 32-76) in the winter, 20 μg/ℓ in the spring (range 5-41) and 10-20 μg/ℓ in the summer. This represents about a threefold average winter enrichment in the surface microlayer relative to the subsurface waters (range 1.4-3.7), and a fivefold spring enrichment. Preliminary data on the summer microlayer samples indicates that the microlayer was enriched to the same extent as it was in the spring.

The chromatograms of the surface film samples from all seasons show various patterns resembling pelagic tar inputs (Butler et al., 1973), probably in the form of small particles (0.1-1000 μm in diameter; Wade et al., 1976). It is also possible that an *Argo Merchant* input is contributing to the observed pattern in the microlayer and the lower boiling alkanes (n-C_{12}-n-C_{22}) are depleted (solubilized?) and appear in the dissolved fraction (see Figure 2). The summer microlayer samples have similar GC patterns to the winter and spring samples, although much enriched in planktonic components, pristane and n-C_{15}. However, the summer "dissolved" hydrocarbon samples do not show the striking n-C_{14}-n-C_{21} alkane predominance as did the winter and spring samples.

Particulate Hydrocarbons. Total hydrocarbon concentrations in the particulate fraction remained fairly constant in the 0.3-5 μg/ℓ range in the winter and spring samples and decreased (0.1-2 μg/ℓ) in the summer. The particulates exhibit several hydrocarbon f_1 patterns (Figures 8A, 9A, 9B) ranging from (1) mid to high molecular weight

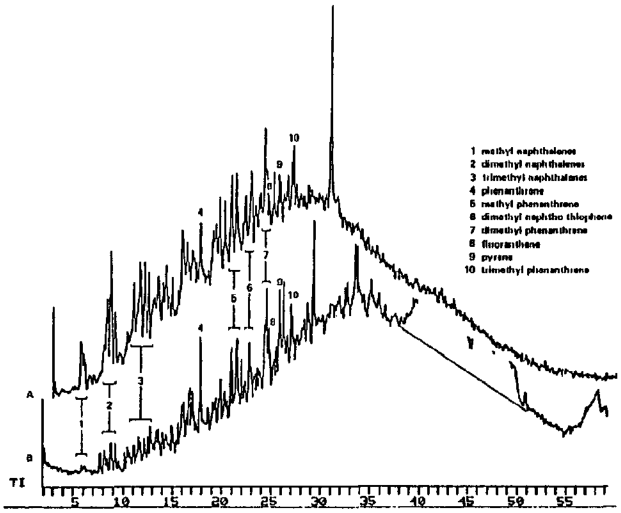

Figure 7. *Reconstructed gas chromatograms. A. Argo Merchant - F_2. B. Winter dissolved - F_2.*

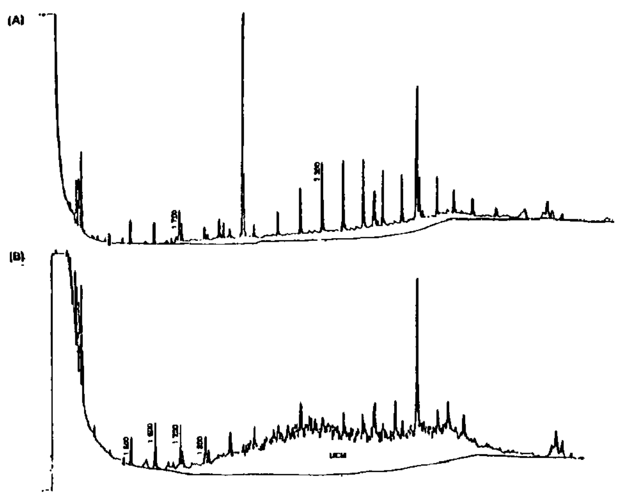

Figure 8. *Particulate hydrocarbons: winter cruise (February 1977). A. f_1 (hexane), Station 1 near bottom. B. f_1 (hexane), Station 32, near bottom.*

n-alkanes, (2) a type 1 input with marked biogenic inputs, and (3) near total zooplankton input. The biogenic input became apparent in the spring and summer samples. A fourth type of distribution (Figure 8B) closely resembles the dissolved hydrocarbon distribution.

The apparent lack of correlation of the dissolved and particulate hydrocarbon concentrations, along with the fact that there is no major winter particulate hydrocarbon increase is puzzling. The explanation may be due to the presence of the so-called dissolved hydrocarbons in (1) a truly dissolved state, (2) a collodial state (solubilized), as well as (3) a particulate ($<0.5\mu$) state (Boehm and Quinn, 1974) which is not trapped under pressure filtration by a Gelman A-E glass fiber filter. Furthermore, the larger particulate material ($\sim 4\ \mu$m and up) may have settled out rapidly (<15 minutes) prior to filtration and hence may not have been filtered out due to an imperfect design of the

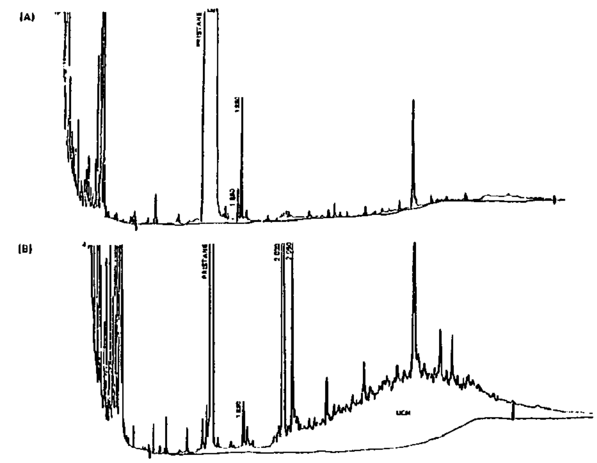

Figure 9. *Particulate hydrocarbons: spring cruise (May 1977). A. f_1 (hexane), Station 42, near bottom. B. f_1 (hexane), Station 32, near surface.*

sampling bottle which permits about 200 ml below the bottle outlet to escape filtration (Gardner, 1977).

Discussion

Hydrocarbon values in the water column of the study region were markedly elevated in the winter of 1977. Is this a normal occurrence due to increased oil-tanker traffic during winter months in this region, or are we seeing a widespread pulse of *Argo Merchant* spilled oil?

To answer this, a further winter sampling of the water column seems appropriate. For now, with the existing data, we must compare the cargo oil with the hydrocarbons found in the samples.

Analysis of an *Argo Merchant* cargo oil sample obtained from J. Milgram (M.I.T.) reveals (Figure 6A) a smooth distribution of n-alkanes ranging from n-C_{11} to n-C_{36} overriding a bimodal UCM in the f_1 fraction. The aromatic (f_2) fraction contains prominent methylated naphthalenes, phenanthrenes and smaller quantities of four- and five-ringed aromatics. Several thiophenes are also observed (Figure 7).

Apparently, the cargo contained approximately 20 percent of a cutter stock, having a component distribution similar to No. 2 fuel (Grose and Mattson, 1977). Due to low sea-water temperatures the spilled oil soon formed large iceberg-like pancakes. However, the rough seas probably allowed for substantial dispersion of oil and hence dissolution of the more soluble fractions in the water column and dispersion as small droplets. Two attempts have been made in our laboratory to simulate the chemical fractionation that may have taken place. In one case the oil was placed on sea water and slow stirring of the aqueous layer achieved. After 24 hours, gas chromatographic analysis of the aqueous phase resulted in an n-alkane distribution closely resembling the n-C_{12}-n-C_{22} n-alkane distribution observed in the winter and spring water samples. In a modification of this experiment, the aqueous layer was stirred turbulently and the oil dispersed as small particles. Upon sampling this aqueous layer, after allowing the mixture to stand, an unaltered *Argo Merchant* f_1 distribution resulted.

These preliminary observations, which will be repeated and refined, suggest that a chemical fractionation of the cargo may have occurred, owing to processes of dispersion, true solution and micellar solubilization (Boehm and Quinn, 1973, 1974). The components most affected were those in the boiling range of a typical No. 2 fuel oil. This fractionation did not affect the aromatic (f_2) distribution as evidenced in Figure 7, where a distribution similar to the f_2 of the oil itself was seen. In studying the solubility behavior of a light distillate, Boehm and Quinn (1974) observed that micellar solubilization affected mainly aliphatic components and that the solubility behavior of the aromatics was independent of the behavior of the aliphatics. A similar process may be involved here. However, more laboratory studies dealing with such subtleties are needed, and, further, detailed chemical studies of spills of opportunity are required to help to confirm what may be very complex solubility and solubilization phenomena associated with spilled oil in sea water.

Without further studies both in the field and in the laboratory, two possibilities remain:

(1) The hydrocarbon concentrations were enhanced in the winter of 1977 because of normal shipping operations associated with bringing oil to the northeast U.S.

(2) The *Argo Merchant* spill affected most of the Georges Bank/Nantucket Shoals region and caused a large increase of the hydrocarbon burden of the water column.

Acknowledgments

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Where the *Argo Merchant* Oil Didn't Go

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Abstract

Between 60 and 90 days after the grounding of the *Argo Merchant*, tar balls were found on shore along Jamestown (RI), Martha's Vineyard, Nantucket, and on Cape Cod from Nauset Beach to Provincetown. Twenty-two of the tar balls were analyzed in our laboratory. Infrared spectra of the tar balls were compared with each other, with the cargo from the *Argo Merchant*, and with the oil loaded onto the lost tanker, the *Grand Zenith*. The fingerprints of many of the tar balls were very similar to each other; however, they were completely different from the fingerprint of the *Argo Merchant* cargo. There was some similarity between the fingerprints of the tar balls and the neat oil loaded onto the *Grand Zenith*.

If these tar balls came from either the *Argo Merchant* or the *Grand Zenith*, they were in the ocean for over one month and the fingerprints could have changed due to "weathering". Thus, we artificially weathered the two neat oils under similar temperature conditions in flowing sea water at the URI aquarium. Weathered samples were collected periodically for one month and their fingerprints compared to those of the tar balls.

The probabilities that the tar balls came from the same source, that they came from the *Argo Merchant*, that they came from the *Grand Zenith*, and that they came from some other source have been determined and are discussed in the report.

Introduction

During February and March of 1977, tar balls were found along the New England coast from Jamestown, Rhode Island, to Provincetown, Massachusetts, including the islands of Martha's Vineyard and Nantucket. Considering the location of the *Argo Merchant* grounding and the time frame, i.e., approximately two months after the tanker broke apart on Nantucket Shoals, there was considerable speculation that the stricken tanker was the source of the tar balls.

Our first involvement with the tar balls was on February 9 when we were notified that oil had come ashore in Jamestown (Rhode Island). We collected 12 tar balls ranging in weight from a few ounces to 15 lbs. During the next two months, we received samples of 30 tar balls collected along the Massachusetts shores. Seventeen of these were from Nantucket. We randomly selected and analyzed 4 of these plus 12 from other sites. Furthermore, we artificially weathered one of the tar balls to study the effects of additional weathering.

Informational data on the tar balls are given in Table 1 and the sites are located in Figure 1. The Nantucket collection dates are approximate, since the samples were collected by the Coast Guard and stored at Woods Hole until April.

Table 1.
Information on Tar Balls

Tar Ball No.	*Site*	*~Date*	*Comment*
1	Jamestown, R.I.	2/9/77	a,~1 lb., composite
2	Jamestown, R.I.	2/9/77	a,~1 lb., outside
3	Jamestown, R.I.	2/9/77	a,~1 lb., inside
4	Jamestown, R.I.	2/9/77	b,~5 lb., inside
5	Jamestown, R.I.	2/9/77	c,~15 lb., inside
6	Martha's Vineyard	2/12/77	
7	Nantucket	2/15/77 to	
8	Nantucket	3/1/77	
9	Nantucket	3/1/77	
10	Nantucket	3/1/77	
11	Nauset Beach	3/1/77	
12	Nauset Beach		No. 11 weath. at GSO
13	Marconi Beach	3/1/77	
14	Marconi/Lecount	3/14/77	
15	Race Pt. Beach	2/10/77	Sewage
16	Race Pt. Light	3/1/77	
17	1000 yds. from Race Pt. Light	3/1/77	
18	Long Pt.	3/12/77	
19	Provincetown Wharf (a)	3/15/77	
20	Provincetown Wharf (b)	3/15/77	
21	Pilgrim Beach (a)	3/12/77	
22	Pilgrim Beach (b)	3/12/77	

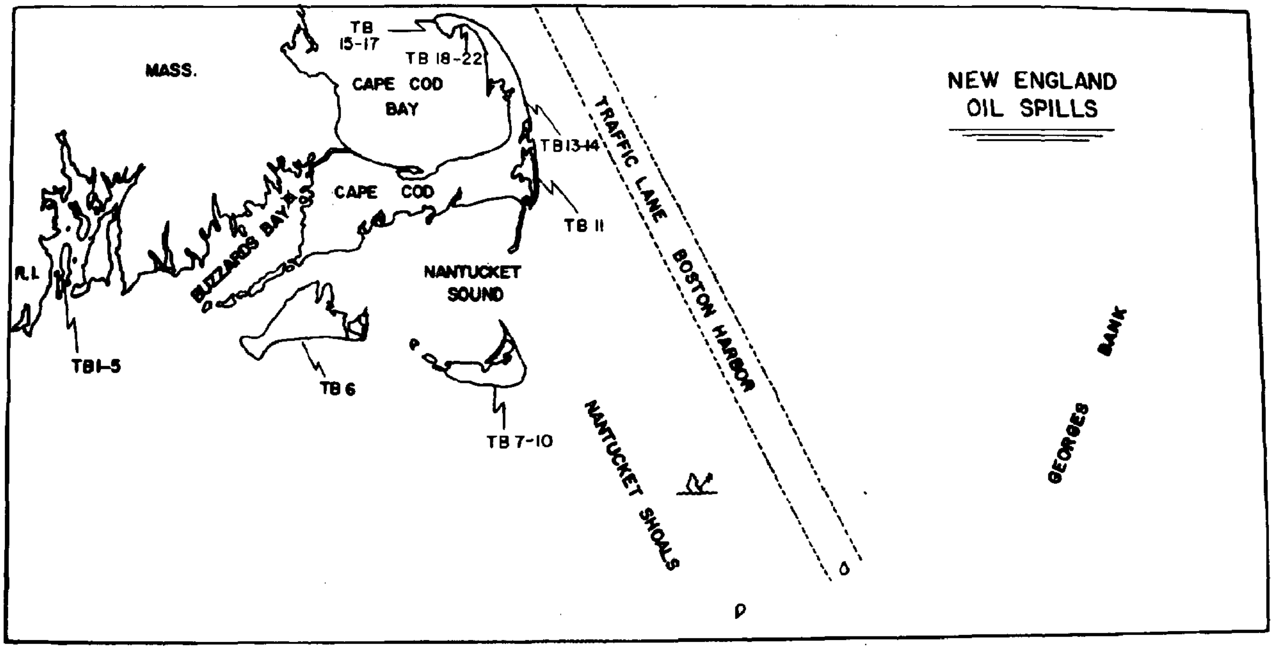

Figure 1. *Map of southern New England with locations of tar balls.*

Experimental

Most of the tar balls contained water, sand and marine debris; thus, all samples were pretreated prior to analysis. Approximately 5 ml of each sample were centrifuged for 2 minutes and the top oil layer transferred to another test tube. Five ml of CCl_4 were added, the sample shaken vigorously and centrifuged for 5 minutes. The top three-quarters of the sample was transferred to another test tube, anhydrous $MgSO_4$ added, and it was centrifuged for another 5 minutes at 35°C. The latter step was repeated several times until all of the water was removed, and then the CCl_4 was removed by evaporation.

The treated samples were placed in demountable AgCl infrared cells with a 0.05 mm spacer and spectra were measured on a Perkin-Elmer Model 521 infrared spectrometer. The digitized spectral data were stored in a computer data file and all data analyses were performed on an IBM 370/60 computer.

Results and Discussion

Probability of Matching Infrared Spectra of Petroleum. Recently, Kileen and Chen (1976) proposed a method for obtaining the probability of matching spilled oil to one or more suspects from infrared spectra of the samples. Their method is an extension of the ratio method developed in our laboratory (Ahmadjian et al., 1976).

In the ratio method, absorbances at 18 frequencies in the spectrum of one sample are ratioed with absorbances at the same frequencies in the spectrum of another sample. The log of each ratio, the average log-ratio, and the differences between each log-ratio and the average log-ratio are determined. Initially, we ratioed the absorbances in the spectrum of each suspect to those in the spectrum of the spill sample; the best match was assigned to the spectrum having the most ratios within 10% of the average. Later, the method was extended to give a single value for estimating the differences between spectra (Brown et al., 1976a). This value is obtained from the sum of the squares of the differences between the log-ratios and the average log-ratio, i.e.,

$$S^2 = \sum_{i=1}^{18} \left(\log \frac{A_i1}{A_i2} - \frac{1}{18}\sum_{i=1}^{18} \log \frac{A_i1}{A_i2}\right)^2$$

where A_{i1} and A_{i2} are the absorbances for the ith band in spectra 1 and 2, respectively. For a perfect match, the value of S^2 would be zero; thus, the magnitude of S^2 reflects the dissimilarity between oils.

We (Brown et al., 1976b) measured spectra of 198 neat and 647 weathered oils (including several weathered samples for each of 80 neat oils). S^2 values for all possible pairs of oils were calculated and placed in one of two categories: same oils (neat and weathered oils from the same origin) and different oils (neat and weathered oils from different origins). There were 5,534 pairs with the two oils originating from the same source, and 345,030 pairs with the two oils from different sources. The pairs in each category were then ordered according to increasing S^2 values, and two histograms for frequency of occurrence vs S^2 in increments of 0.01 were plotted.

The histograms provided distributions for pairs of oils from the same sourses and for pairs from different sources. Killeen and Chien (1976) used these distributions to determine the probabilities of guilt for each suspect in a spill case and the probability that a sample from the "true spiller" was not included. Their method is based on Bayes Theorem and is described completely in their report.

In the present report it is important to note that the distributions used to obtain the probabilities are based on all types of oils, i.e., they are comprised of light through heavy crudes, fuels and lubricating oils. This tends to give slightly higher probabilities especially at the low end

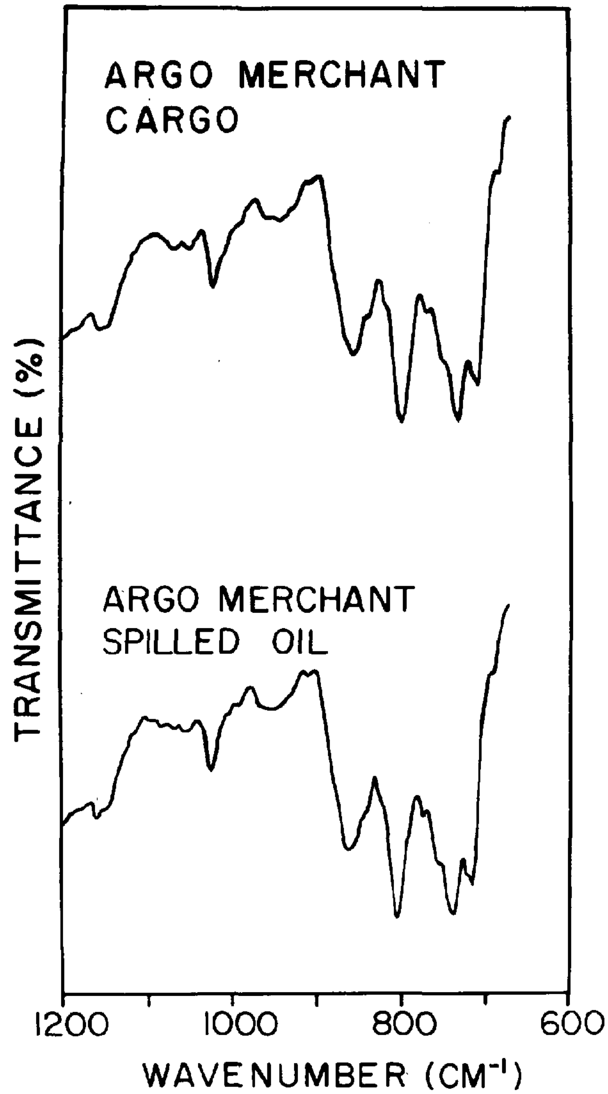

Figure 2. *Infrared spectra of the Argo Merchant cargo and of the spilled oil collected 2 days after the spill.*

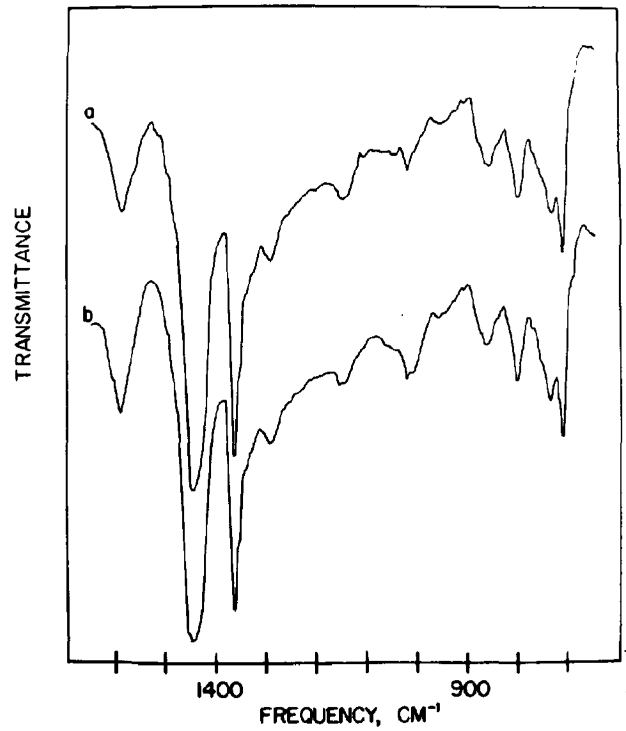

Figure 3. *Infrared spectra of tar balls: a, Jamestown, and b, Martha's Vineyard.*

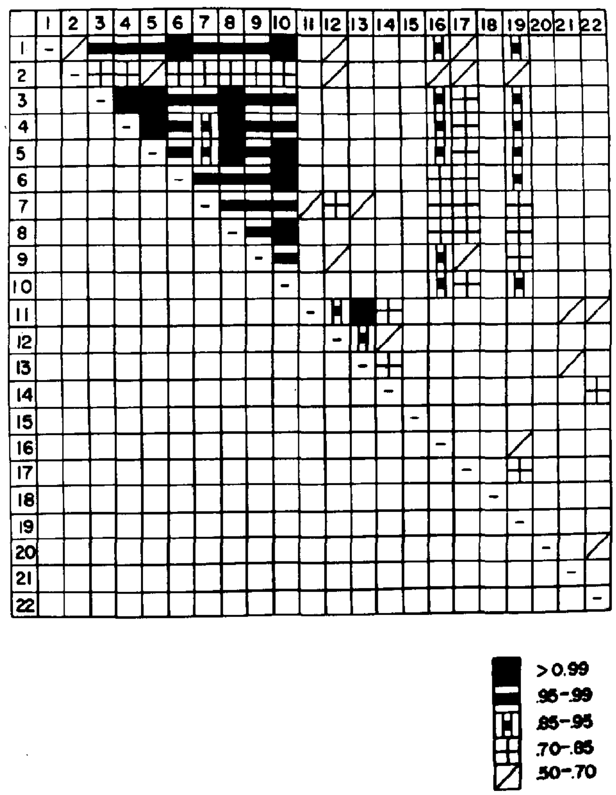

Figure 4. *Probabilities of tar balls matching.*

of the 0 to 1 probability scale. For example, infrared fingerprints of two No. 6 fuels may be completely different and we would expect that the probability that they match would be close to 0.0. However, since they are both No. 6 fuels, their fingerprints will be more similar than the fingerprints of a No. 6 and a No. 2 fuel. Thus, in many cases, the probability that two different No. 6 oils match will be higher than expected because they are the same type of oil.

Argo Merchant Spill. Infrared spectra of the *Argo Merchant* cargo and of the spilled oil collected two days after the tanker broke apart are shown in Figure 2. (These samples were obtained from Dr. Jerome Milgram, MIT.) When the digitized spectrum of the spilled oil was compared with that of the cargo, the following probabilities were obtained:

	Probability
Argo Merchant	0.986
Another Source	0.014

Table 2.
Probabilities of Tar Balls Matching
(In % Units)

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*	*20*	*21*	*22*
1	–	66	96	96	97	99	95	97	97	99	46	55	43	20	0	86	66	16	89	16	22	18
2		–	76	70	67	79	77	77	71	71	45	56	41	33	0	56	51	16	58	18	19	20
3			–	96	100	97	96	99	97	98	38	45	36	18	0	90	77	20	91	17	19	18
4				–	100	98	93	100	97	99	33	41	31	18	0	87	83	17	90	16	18	17
5					–	97	93	99	98	100	35	42	34	18	0	90	80	20	91	14	18	18
6						–	98	98	97	99	47	60	44	22	0	84	76	17	89	18	22	18
7							–	95	98	95	55	72	53	26	0	74	73	16	82	18	28	19
8								–	96	99	38	48	35	19	0	84	84	19	84	16	17	18
9									–	97	45	50	42	21	0	91	63	16	73	17	23	18
10										–	40	48	38	19	0	91	76	18	86	16	20	18
11											–	94	99	81	0	33	23	21	33	34	55	59
12												–	94	57	0	31	37	18	44	32	39	36
13													–	80	0	31	23	19	33	32	54	48
14														–	0	18	18	21	18	44	36	71
15															–	0	0	0	0	0	0	0
16																–	25	16	58	15	20	19
17																	–	0	70	16	17	17
18																		–	22	19	19	43
19																			–	15	18	17
20																				–	23	55
21																					–	44
22																						–

The deviation from 1.0 is possibly due to weathering of the spilled oil.

Intercomparison of Tar Balls. Infrared spectra of the 22 tar balls listed in Table 1 were measured and the digitized fingerprints stored in a computer data file. Many of the spectra had similar contours and some were almost identical as is shown in Figure 3. The spectrum of each tar ball was compared with that of each of the others and the probability that they came from the same source is given in Table 2. The results are categorized according to magnitude in Figure 4.

All samples from Jamestown, Martha's Vineyard and Nantucket have probabilities >0.85 of being identical except for sample 2 from Jamestown. This was a sample of the outside layer of a tar ball, and the differences reflect excessive weathering on the surface. In addition to samples 1-10 being from the same source, the probabilities that samples 12, 16, 17 and 19 came from this source are >0.5. Furthermore, tar balls 11 and 13 are virtually identical ($P = 0.99$).

It should be mentioned that the differences between many of the tar balls could be due to weathering and that this effect is more pronounced on the surface of the tar balls. Many of the tar balls from Cape Cod were very small and these could have been subjected to extensive weathering.

Tar Balls and the Argo Merchant Cargo. The infrared spectral fingerprint of the *Argo Merchant* oil is compared to that of the Martha's Vineyard tar ball in Figure 5. The general contours of the spectra are entirely different. We treated each of the 22 tar balls as a spill sample and determined the probability that each came from the

Table 3.
Probability of Tar Balls Originating From *Argo Merchant* Cargo
(In % Units)

Tar Ball	*Neat*	*Argo Merchant Cargo* 3 Days Weathered	*Argo Merchant Cargo* 10 Days Weathered
1	22	18	18
2	18	25	18
3	21	5	18
4	19	0	18
5	20	0	18
6	20	7	18
7	19	19	18
8	20	22	18
9	21	23	18
10	21	20	18
11	32	18	32
12	23	18	27
13	27	19	27
14	18	18	18
15	0	0	0
16	21	0	18
17	15	17	16
18	18	16	18
19	18	25	18
20	18	28	21
21	19	18	22
22	22	18	28

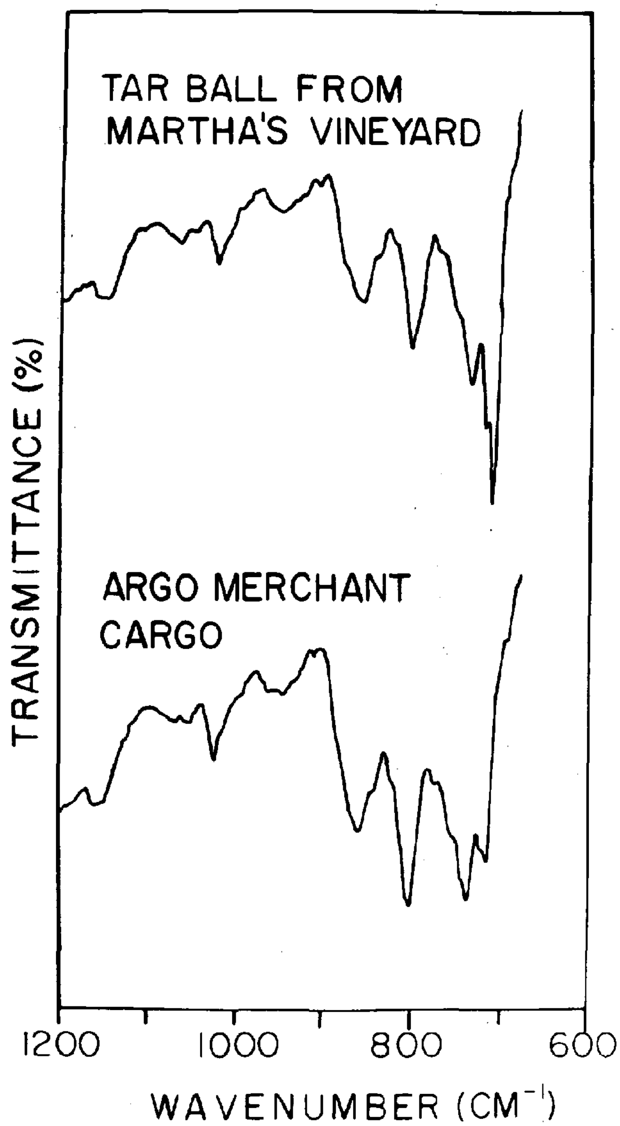

Figure 5. *Infrared spectra of tar ball from Martha's Vineyard and Argo Merchant cargo.*

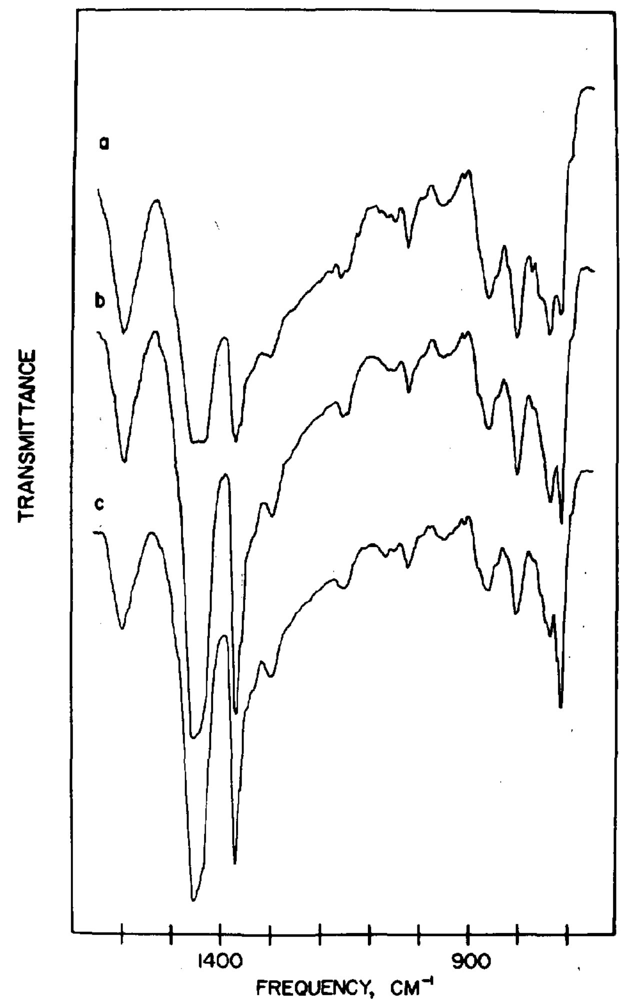

Figure 6. *Infrared spectra: a, Argo Merchant cargo, b, Grand Zenith oil, and c, Martha's Vineyard tar ball.*

cargo. The results given in Table 3 show that only sample No. 11 (Nauset Beach) had a probability of matching>0.3; most were <0.2. The spectrum of the cargo and the tar balls (except for sample 15) were characteristic of No. 6 fuel oils. Thus, these finite probabilities reflect the fact that the samples are the same type of oil.

If the tar balls came from the *Argo Merchant*, they were "weathered" in the Atlantic for almost 2 months; thus, we weathered some of the cargo oil at the URI aquarium for one month and periodically analyzed samples. In most cases, the spectra of the tar balls and the weathered *Argo Merchant* tar balls became less similar. The probabilities of matching for the 3 and 10 day samples are also given in Table 3.

Tar Balls and the Grand Zenith Oil. The tanker *Grand Zenith* disappeared somewhere off the New England coast on the way from Teeside, England to Fall River, Massachusetts during January 1977; thus, its cargo was also a possible source of the tar balls. The U.S. Coast Guard R & D Center supplied us with a sample of the oil loaded aboard the *Grand Zenith.* We measured infrared spectra of the neat oil and of samples collected periodically during one month of weathering at the URI aquarium. The infrared spectrum of the *Grand Zenith* oil is compared with the *Argo Merchant* cargo and the Martha's Vineyard tar ball in Figure 6.

The probabilities obtained when comparing the spectra of the neat and 7 weathered samples to the tar balls are given in Tables 4a and 4b. The probabilities run as high as 0.83 when the neat oil is compared to tar balls Nos. 3 and 4; however, the highest probability (90%) was obtained from matching the 14 day weathered sample with tar ball No. 11 from Nauset Beach (see Figure 7 for spectra). Other tar balls found in this area (Nos. 13 and 14) have probabilities of ~ 0.85 of matching the weathered *Grand Zenith* oil.

According to the probabilities given in Table 4, the tar balls can generally be placed into three categories: i) those with high probabilities of matching the neat or short term weathered samples, ii) those with high probabilities of matching the long term weathered samples, and

Table 4a.
Probability of Tar Balls Originating From *Grand Zenith* Cargo
(In % Units)

Tar Ball	*Grand Zenith Cargo Weathered (Days)* 0	1	2	4
1	74	77	75	51
2	45	45	52	55
3	83	87	86	66
4	83	87	88	69
5	82	88	86	63
6	73	75	76	57
7	60	65	70	52
8	76	81	81	58
9	69	73	73	44
10	79	83	83	55
11	36	35	38	31
12	38	38	42	41
13	32	33	35	30
14	18	18	18	18
15	0	0	0	0
16	75	78	77	40
17	33	37	40	44
18	14	16	16	20
19	71	75	74	81
20	16	16	16	15
21	18	18	20	19
22	18	18	18	18

Table 4b.
Probability of Tar Balls Originating From *Grand Zenith* Cargo
(In % Units)

Tar Balls	*Grand Zenith Cargo Weathered (Days)* 7	14	21	28
1	73	55	26	27
2	58	47	33	34
3	77	50	22	24
4	75	49	20	21
5	76	47	20	21
6	77	58	29	29
7	70	63	35	34
8	72	47	23	23
9	74	61	29	30
10	78	54	25	26
11	55	90	86	87
12	51	73	64	58
13	47	84	81	83
14	23	41	87	77
15	0	0	0	0
16	85	58	23	28
17	32	24	18	18
18	17	19	18	21
19	59	37	18	20
20	18	22	37	30
21	27	46	61	63
22	22	40	58	64

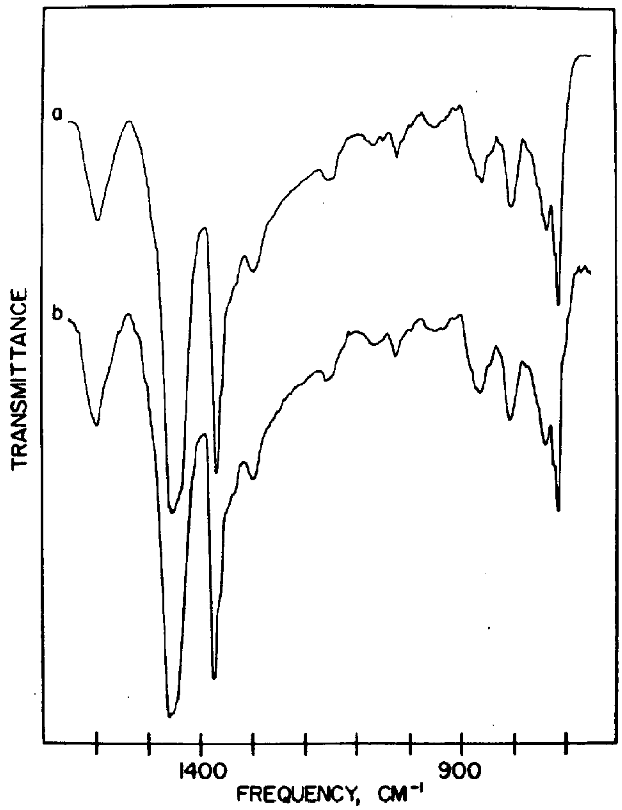

Figure 7. *Infrared spectra: a, tar ball from Nauset Beach, and b, Grand Zenith oil weathered 14 days.*

iii) those with low probability matches. Samples 1, 3-10, 16 and 19 fall in category i, samples 11-14, 21 and 22 in category ii, and the rest in iii.

Conclusions

The present study showed conclusively that the tar balls found along the New England coast after the *Argo Merchant* incident were not from the stricken tanker. Many of the tar balls had similar infrared spectra and there is a high probability that a number of these came from the same source. Finally, there is a reasonably high probability that some of the tar balls originated from the stricken tanker *Grand Zenith*. It should be noted that the tar balls were compared with the oil loaded onto the *Grand Zenith*, and not to the oil actually contained in the tanker. The composition of the oil in the tanker could have been slightly different due to residues in the tanker from previous shipments.

Acknowledgments

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Hydrocarbon Patterns in Some Marine Biota and Sediments Following the *Argo Merchant* Spill

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Abstract

Over 60 samples of marine biota or sediments collected in response to the *Argo Merchant* oil spill were analyzed for hydrocarbons by glass capillary gas chromatography (GC). High resolution GC patterns of the saturated hydrocarbons extracted from the samples were compared with the corresponding pattern from the *Argo Merchant* cargo. The stomach contents from one cod sample and one windowpane flounder sample gave GC patterns which compared closely to the cargo pattern. Analogous comparisons of the aromatic hydrocarbons confirmed only the correlation for the sample from the cod. When GC patterns failed to match closely, objective pattern matching procedures were devised to rank the patterns of the major sample hydrocarbons for their similarity to the reference pattern. Similarity between sample and reference relative abundance patterns was expressed as the percent of the sample hydrocarbons (among those measured) whose individual relative abundance fit the reference relative abundance within a specified tolerance. Calculations were based on the assumption of either (a) no weathering effects on the hydrocarbon distribution patterns, or (b) significant, but indeterminate, alteration of the distribution of the more volatile and water-soluble hydrocarbons.

Introduction

The grounding of the tanker *Argo Merchant* on Nantucket Shoals in December 1976, and its subsequent breakup with a total loss of 7.7 million gallons of No. 6 fuel oil cargo, set in motion a number of scientific activities noted by Grose and Mattson (1977). Their report describes sampling cruises by the National Marine Fisheries Service (NMFS) and by the University of Rhode Island (URI) which procured samples of marine biota and sediments for the analyses discussed here. We have analyzed more than 60 of these samples for saturated and aromatic hydrocarbons to elicit evidence of contamination by the spilled *Argo Merchant* cargo. A sample of cargo oil collected from the wreck by Prof. J. Milgram of M.I.T. (Grose and Mattson, 1977) served as the reference.

Petroleum and petroleum-based fuel oils contain a broad range of compounds, mostly hydrocarbons. When such complex mixtures are released into the marine environment, they are subject to a number of physical, chemical, and biological processes known collectively as "weathering". Depending on many factors, these processes can alter the composition of the mixture of compounds (distribution pattern) constituting a spilled oil, frequently beyond recognition in terms of the original pattern (Clark and MacLeod, 1977). To some extent these effects can be compensated for (Bentz, 1976), but they need to be understood much better before compositional data on hydrocarbons from environmental samples can be interpreted unambiguously with respect to sources of oil contamination (Farrington and Medeiros, 1975; Malins, 1977). Despite such reservations, it is still possible to derive inferences linking a suspected source of contamination with a sample extract, if finely discriminating spectral or chromatographic characteristics of their respective hydrocarbon fractions agree. As one example, Adlard et al. (1972) have demonstrated that high resolution gas chromatography (GC) can provide finely detailed characterizations of hydrocarbon fractions to differentiate oils.

Establishing a relationship between hydrocarbons from an environmental sample and a suspected source of oil contamination becomes increasingly difficult as environmental processes alter the distribution pattern of hydrocarbons from environmental samples. Since this is a common problem, it is important to investigate detailed pattern matching procedures for a better understanding of the fate of hydrocarbons introduced into the marine environment, including their transformations throughout the food web. Oil pattern matching methodology based on comparisons of spectral or chromatographic proper-

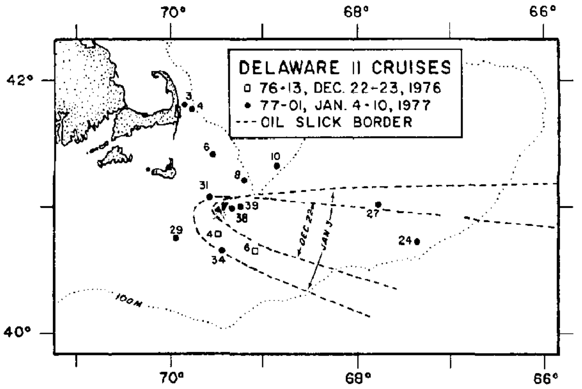

Figure 1. *Collection locations for samples of marine biota taken during cruises of the R/V Delaware II (Grose and Mattson, 1977).*

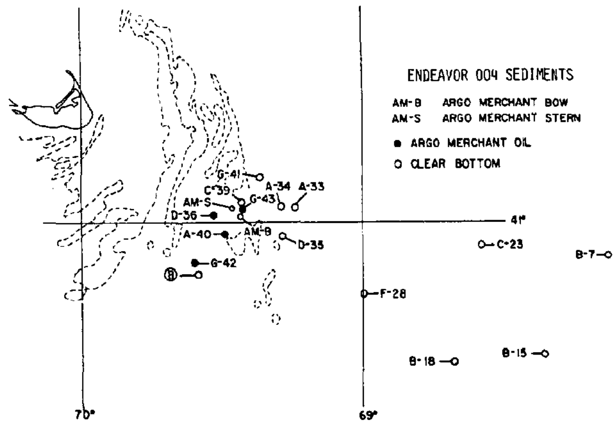

Figure 2. *Collection locations for samples of sediments taken during cruise 004 of the R/V Endeavor (Grose and Mattson, 1977).*

ties has been reviewed by Bentz (1976). Recent developments have been reported from the workshop convened by Chien and Killeen (1976). Interestingly, little of this work has exploited the power of high resolution (i.e., capillary) GC, in spite of the superior separations demonstrated on complex hydrocarbon mixtures a decade ago (MacLeod, 1968; Modzeleski et al., 1968) or subsequently (Adlard et al., 1972).

In early oil pattern matching work utilizing a modified GC capillary, Zafiriou (1973) employed a support-coated open-tubular (SCOT) column to obtain abundance data on four alkane descriptors in his procedure for comparing oil-rich samples. Clark and Jurs (1975) incorporated additional descriptors from Zafiriou's chromatograms to test computerized pattern matching procedures for alkanes. The SCOT column is also used in Flanigan's (1976) pattern matching routines.

Now that more high resolving glass capillary GC columns and related chromatographs are available commercially, detailed compositional characterizations of complex hydrocarbon mixtures have become sufficiently routine that these analyses can be readily automated (MacLeod et al., 1976, 1977). Hence, it is timely that the wealth of compositional information obtainable by glass capillary GC receives due consideration in oil matching research.

In this study, detailed GC patterns of the saturated and aromatic hydrocarbon fractions obtained from environmental samples were compared with reference GC patterns from the *Argo Merchant* cargo. If the sample and reference high resolution GC patterns visually corresponded closely in the fine details, a probable match was indicated. When sample and reference high resolution GC patterns differed sufficiently to eliminate the possibility of an obvious match, the excellent resolution still assured confidence in major hydrocarbon abundance measurements and their relative freedom from interferences. Under these circumstances, we employed two simple arithmetical procedures to rank the major hydrocarbon distribution patterns according to their similarity to the *Argo Merchant* reference pattern.

Methods and Materials

Samples of marine biota were collected during two cruises of the R/V *Delaware II* (Figure 1) using standard NMFS groundfish survey procedures (Grose and Mattson, 1977). Samples of marine sediments in the vicinity of the wreck were collected by URI on the cruise of the R/V *Endeavor* shown in Figure 2 (Grose and Mattson, 1977). All samples were frozen until analyzed. In general, samples of biota were composited from three or more individuals of a species. These samples were homogenized, digested with alkali, solvent extracted, chromatographed on silica gel, analyzed by glass capillary GC, and confirmed by mass spectrometry (MS) according to published procedures (MacLeod et al., 1976). Sediment samples also were analyzed according to these procedures, except that they were extracted twice by methanol and three times by methylene chloride/methanol (2/1) according to Brown et al. (1978). Hexamethylbenzene was used as the GC internal standard (IS). Previous studies have shown that losses of individual hydrocarbons are generally less than 30% in sample workup, and that relative standard deviations of ca. 20% can be attained for abundance measurements for most hydrocarbons (MacLeod et al., 1976).

Gas chromatograms of the saturated and aromatic hydrocarbons from the samples were compared with the corresponding reference chromatogram from the *Argo Merchant* cargo. Abundance levels were calculated for 24 major alkanes in the saturated hydrocarbon fraction. This included the *n*-alkanes from *n*-$C_{10}H_{22}$ to *n*-$C_{31}H_{64}$, plus pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane). Abundance levels were also calculated for 18-21 major arenes in the aromatic hydrocarbon fraction. After correcting for analytical background levels, the alkane and arene abundances were normalized relative to tetracosane (*n*-$C_{24}H_{50}$) and phenanthrene ($C_{14}H_{10}$) abundances, respectively. The resulting major alkane or arene relative abundance profile for a sample constitutes the relative distribution pattern of these major hydrocarbons from that sample.

The major hydrocarbon distribution patterns from the samples were ranked for their similarity to the reference. This was expressed as the percent of compounds used in the distribution pattern (excluding the normalizing compound) whose individual relative abundance fell within a $\pm 1/3$ tolerance of the corresponding reference relative abundance. In addition, the major alkanes from the biota were analogously compared with the cargo alkanes using 90% confidence intervals cal-

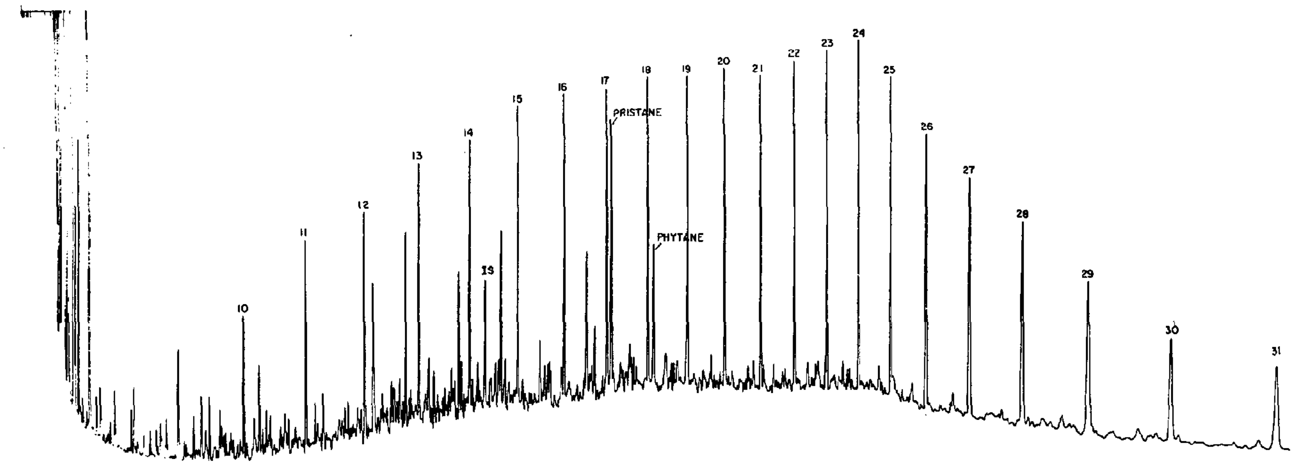

Figure 3. *High resolution gas chromatogram of saturated hydrocarbons extracted from a sample of the Argo Merchant cargo collected by Prof. J. Milgram (Grose and Mattson, 1977). Numbers denote normal alkane carbon chain lengths. 20m x 0.25mm WCOT glass column coated with SE-30. 2 µl splitless injection, split (10:1) after 12 seconds with 14 psi helium carrier gas. Isothermal for first 5 minutes at 40°C, programmed from 40° to 270°C at a rate of 4°C/minute. Internal standard (IS): hexamethylbenzene.*

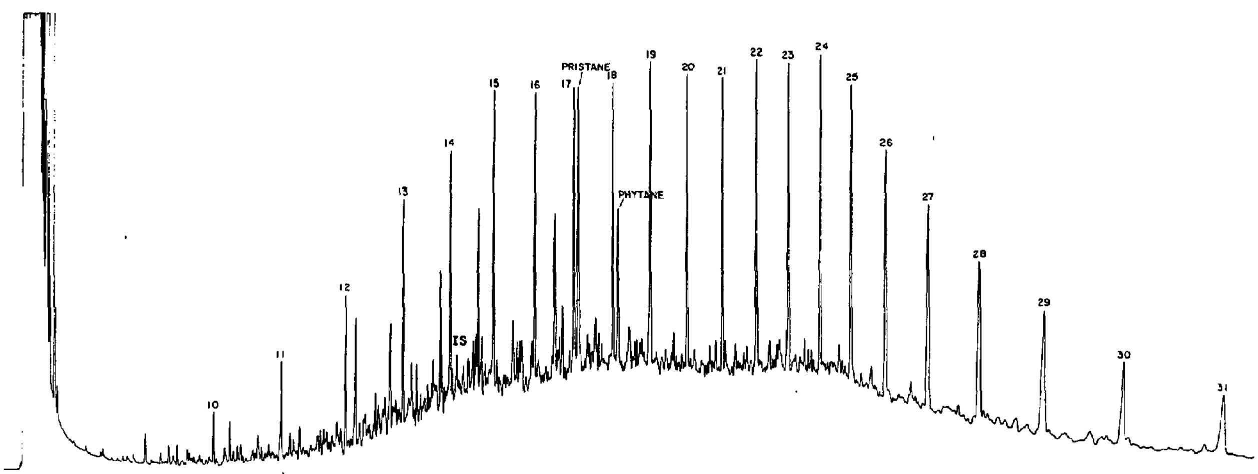

Figure 4. *High resolution gas chromatogram of saturated hydrocarbons extracted from the stomach contents of cod collected on a cruise of the R/V Delaware II (DE 77-01, station 29). Numbers denote normal alkane carbon chain lengths. Conditions same as for Figure 3.*

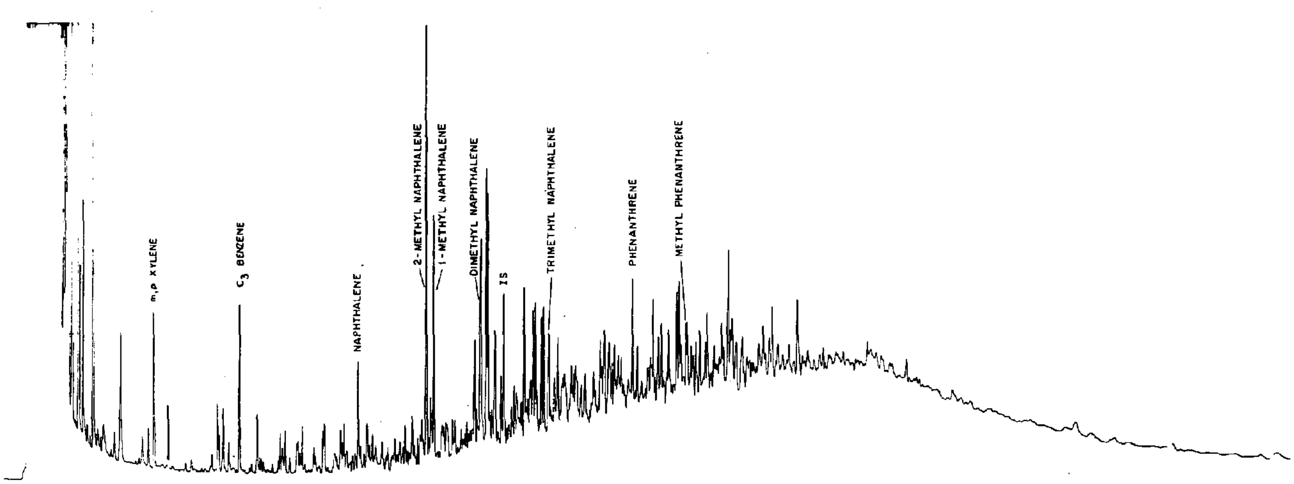

Figure 5. *High resolution gas chromatogram of aromatic hydrocarbons extracted from a sample of the Argo Merchant cargo collected by Prof. J. Milgram (Grose and Mattson, 1977). Conditions same as for Figure 3. Identified compounds confirmed by mass spectrometry.*

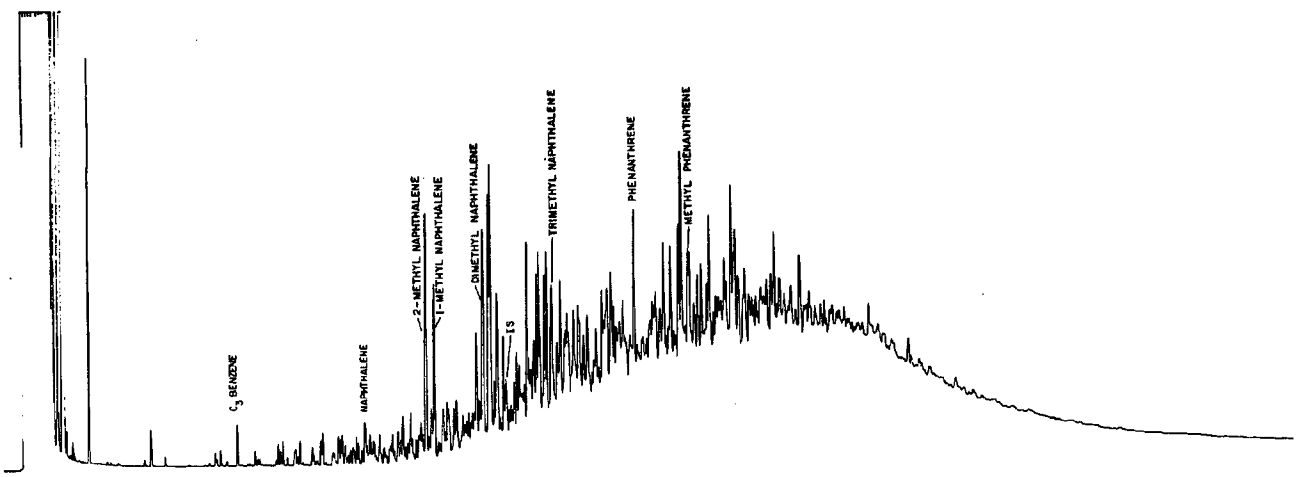

Figure 6. *High resolution gas chromatogram of aromatic hydrocarbons extracted from the stomach contents of cod collected on a cruise of the R/V Delaware II (DE 77-01, station 29). Conditions same as for Figure 3. Identified compounds confirmed by mass spectrometry.*

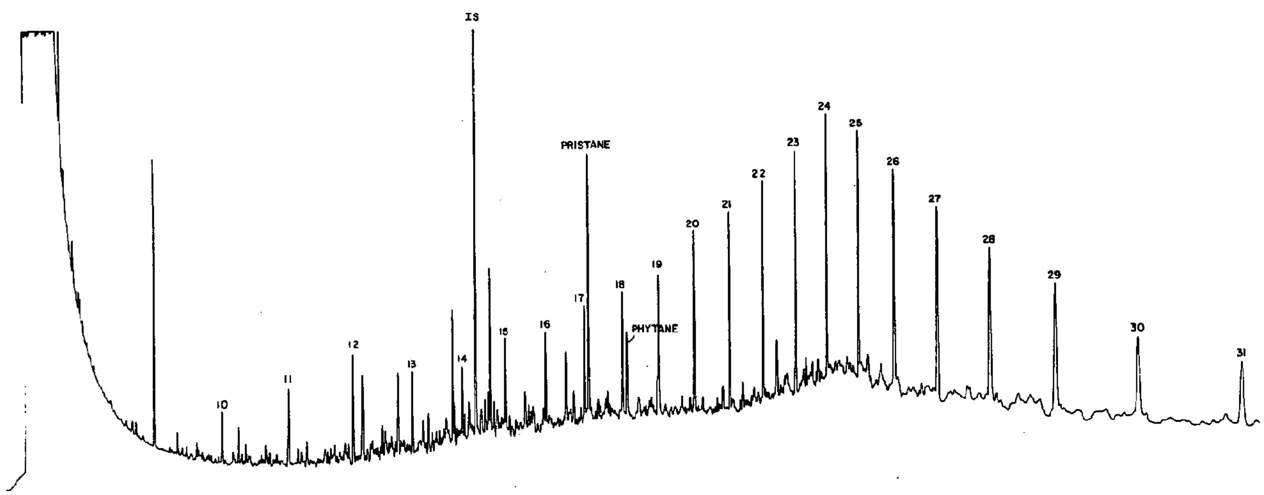

Figure 7. *High resolution gas chromatogram of saturated hydrocarbons extracted from the stomach contents of windowpane flounder collected on a cruise of the R/V Delaware II (DE 76-13, station 4). Numbers denote normal alkane carbon chain lengths. Conditions same as for Figure 3.*

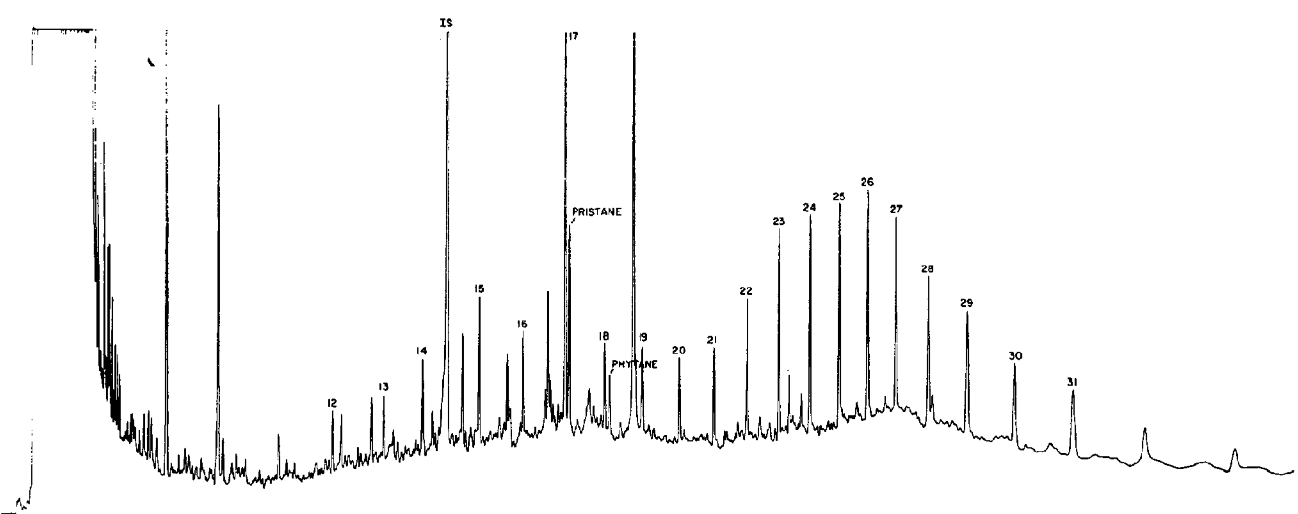

Figure 8. *High resolution gas chromatogram of saturated hydrocarbons extracted from the stomach contents of cod collected on a cruise of the R/V Delaware II (DE 77-01, station 38). Numbers denote normal alkane carbon chain lengths. Conditions same as for Figure 3.*

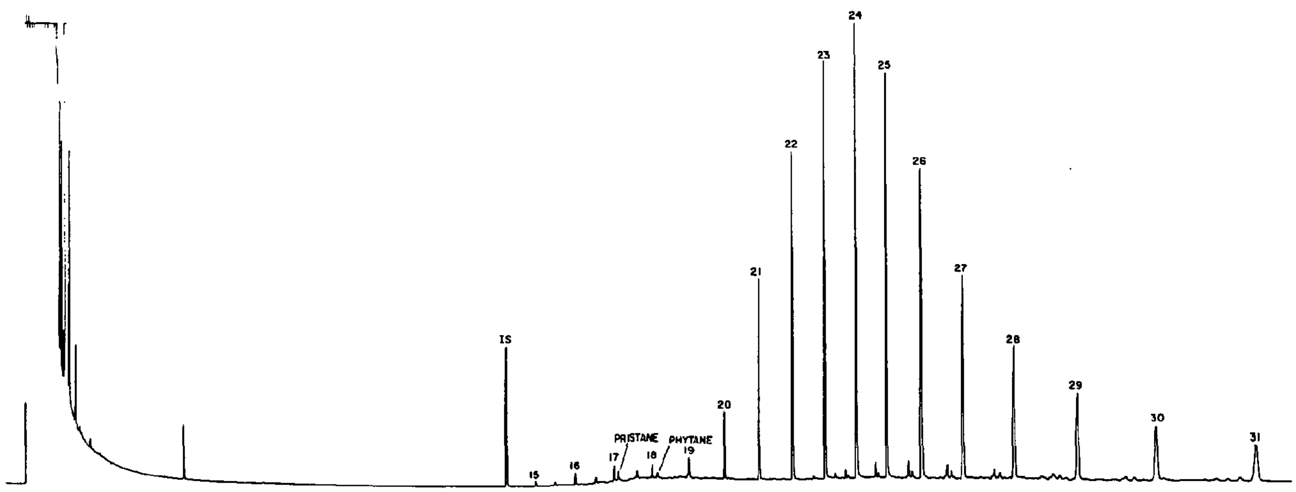

Figure 9. *High resolution gas chromatogram of saturated hydrocarbons extracted from the stomach contents of silver hake collected on a cruise of the R/V Delaware II (DE 77-01, station 24). Numbers denote normal alkane carbon chain lengths. Conditions same as for Figure 3.*

culated from quadruplicate analyses of the reference oil via the analytical procedure for the biota.

Results and Discussion

High Resolution Gas Chromatography. In our analyses of the hydrocarbons from marine biota and sediments collected in response to the *Argo Merchant* oil spill (Grose and Mattson, 1977), the most direct evidence of contamination by the *Argo Merchant* cargo was found in the GC patterns (gas chromatograms) of the hydrocarbons from three samples of fish stomach contents. The hydrocarbons from the stomach contents of the cod collected on cruise DE 77-01, station 29, correlated best with the hydrocarbons from the cargo reference sample. Figure 3 shows the high resolution GC pattern of the saturated hydrocarbons from the reference. The corresponding GC pattern from the cod stomach contents is shown in Figure 4. Both finely detailed GC patterns show extensive qualitative and semi-quantitative agreement in their distribution of compounds. A similar correspondence was found between the aromatic hydrocarbons of this sample and the reference. Figure 5 shows the high resolution GC pattern of the *Argo Merchant* aromatic hydrocarbons; its counterpart from the cod stomach contents appears in Figure 6. Both saturated and aromatic hydrocarbons compare so well with those of the cargo sample that it would be difficult to refute the contention that the stomach contents of cod from cruise DE 77-01, station 29, had been contaminated with oil from the *Argo Merchant* spill, even though it apparently was collected outside the perimeter of the surface slick (Figure 1).

The saturated hydrocarbons from the stomach contents of a sample of windowpane flounder collected on cruise DE 76-13, station 4, gave a GC pattern (Figure 7) which also corresponded well with the reference GC pattern (Figure 3). However, the level of individual major alkanes (10-100 ppb) was much lower than that of the cod stomach (10-30 ppm) discussed above, and few of the major arenes could be detected and measured with certainty. Thus, while it would appear that the windowpane flounder could also have ingested some of the spilled *Argo Merchant* cargo, the evidence is not as strong as in the previous case.

The high resolution GC pattern of the saturated hydrocarbons from another sampling of cod stomach contents (cruise DE 77-01, station 38) gave major alkane levels comparable to the windowpane flounder above, but its resemblance to the reference GC pattern (Figure 8 vs. Figure 3) was poorer. The aromatic hydrocarbon GC response was too weak for pattern comparison. In another case of interest, the stomach contents of a silver hake sample (cruise DE 77-01, station 24) showed high levels (10 ppm) of certain residual paraffins in its GC pattern (Figure 9), although it is not clear how they could be related to the *Argo Merchant* cargo. Six of the major cargo arenes were present at ppm levels, but the aromatic hydrocarbon GC pattern bore no resemblance to Figure 5. None of the remaining 33 samples of biota or 25 samples of sediment gave high resolution GC patterns of their saturated or aromatic hydrocarbons which could be visually related to Figure 3 or Figure 5, respectively.

Major Hydrocarbon Pattern Ranking. As demonstrated above, the high resolution gas chromatograms of the saturated and aromatic hydrocarbon fractions from environmental samples can contain a wealth of information useful for visually documenting detail by detail comparisons with a known reference source of oil contamination. However, when the GC patterns under comparison fail to correspond well in a logical way with regard to conceivable environmental alterations (e.g. weathering), interpretations on the basis of these visual, subjective comparisons become difficult to articulate meaningfully. In view of these uncertainties, some sort of objective scale for ranking these less definitive comparisons might prove useful. In pursuing this issue in an elementary way, we elected to concentrate on sets of major hydrocarbon compounds since they can be measured readily and with confidence by high resolution glass capillary GC. The major hydrocarbon abundance data so obtained was converted to a common relative scale by normalizing this data with respect to a "reliable" member of the set. The resulting set of relative abundances of the major alkanes or arenes (listed according to position in the GC pattern)

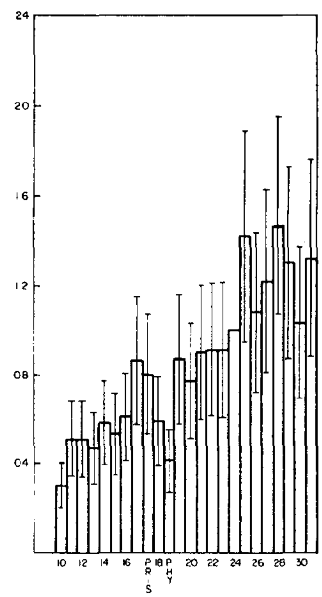

Figure 10. *Relative abundances of pristane, phytane, and n-alkanes, normalized to the abundance of tetracosane in an extract of a sample from the Argo Merchant cargo.* I *indicates upper and lower bounds of ±⅓ tolerance used for comparing sample relative abundances to this pattern.*

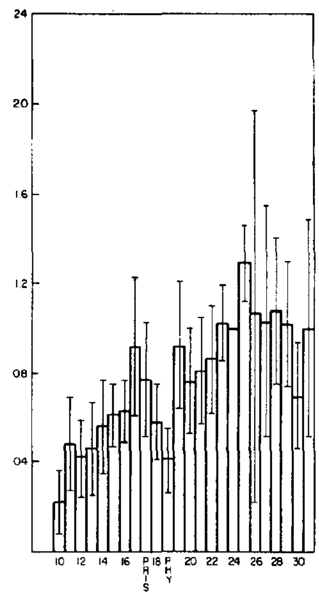

Figure 11. *Relative abundances of pristane, phytane, and n-alkanes, normalized to the abundance of tetracosane in an extract of a sample from the Argo Merchant cargo.* I *indicates upper and lower bounds of 90% confidence intervals used for comparing sample relative abundances to this pattern.*

constitutes a distribution pattern of the set.

The choice of a reliable normalizing compound was relatively straightforward in the case of the major alkanes. Tetracosane (n-$C_{24}H_{50}$) is within the molecular weight range for low susceptibility to evaporation and dissolution relative to more volatile alkanes, especially under the wintry conditions of the *Argo Merchant* oil spill. Being an even-carbon numbered n-alkane, it is less likely to have been contributed from immediate biological sources. Finally, an examination of the high resolution gas chromatograms revealed that it appeared to be free of interference by adjoining peaks. This would not be true for octacosane which may be merged with a branched or cyclic hydrocarbon (MacLeod et al., 1976, 1977). Phenanthrene was chosen for normalization among the arenes because it was the least volatile of the major arenes found in the *Argo Merchant* cargo; the others were too volatile and water-soluble to merit serious consideration.

The distribution patterns of the alkane and arene relative abundances were plotted in bar-graph form for easy visual comparisons. Since exact fit of the relative abundances between sample and reference was not expected, a tolerance span associated with the reference relative abundance was employed to rank-order inexact fits of the sample relative abundance values. For simplicity, this ranking was expressed as the percentage of compounds within the set (excluding the normalizing compound) which were within a specified tolerance.

Within practical limits, the order of ranking of the sample relative abundance patterns with respect to the *Argo Merchant* reference pattern did not depend upon the size of the tolerance spans. For example, the order of ranking was similar whether ±⅓ or ±½ tolerances were used. We employed a ±⅓ tolerance span around each reference relative abundance value based on the following considerations:

(a) The relative standard deviation of the analytical procedure (MacLeod et al., 1976) averages ±15 to ±20% for most environmental samples.

(b) In comparing the results of two analyses (e.g., sample vs. reference alkanes), the overall uncertainty contribution is roughly additive, or ±30 to ±40%.

(c) A tolerance span of ±⅓ approximates ±30 to ±40%.

Application of this pattern ranking procedure to the sample arenes ended when it became obvious that the measurable levels of the gas chromatographable arenes found in most of the samples were insufficient for useful comparisons. The remaining discussion therefore centers on the major alkanes found in the cargo, viz., the n-alkanes from C_{10} to C_{31}, plus the isoprenoidal alkanes, pristane and phytane. The reference relative abundance pattern from the *Argo Merchant* cargo sample with its ±⅓ tolerances is shown in Figure 10.

The percentage of alkanes in the set whose relative abundances fit the reference pattern within the ±⅓ tolerance (Figure 10) is listed for the samples of biota in Table 1 under "% Fit". Three of the 37 samples analyzed registered a 57-61% fit. These results are from the stomach contents of the fish which also gave the best visual GC pattern comparisons above. Two samples registered a 30-39% fit and 11 samples registered a 13-22% fit, including the heavily contaminated silver hake stomach contents (17% fit). The remaining 19 samples failed to indicate measurable alkane levels by our analytical procedure.

Since certain assumptions were made with the ±⅓ tolerance criterion, an alternate method of setting the tolerance span was investigated. To place the alkane

Table 1. Percent fit of alkane relative abundance patterns of *Argo Merchant* cargo vs. marine biota samples by the ±1/3 tolerance and the 90% confidence intervals; median (chi-square test), and diversity index (t-test) results.

Sample	Cruise	Station	% Fit 1/3	% Fit 90%	Median Chi-square	Diversity (t-test)
Cod: stomach contents	77-01	29	57	70	+	+
Haddock: flesh	77-01	8	22	13	+	
Silver hake:						
flesh	77-01	3	17	26		
stomach contents			39	30		
Yellowtail flounder:						
flesh	77-01	3	22	22	+	
Winter flounder:						
stomach contents	77-01	3	22	13	+	
Cod:						
flesh	77-01	38	13	13	+	
stomach contents			57	65	+	+
Haddock:						
stomach contents	77-01	27	30	26	+	
Silver hake:						
flesh	77-01	24	17	26	+	
stomach contents			17	22	+	
Winter flounder:						
flesh	77-01	31	17	22	+	
stomach contents			13	17	+	
Windowpane flounder:						
stomach contents	76-13	4	61	65	+	+
Sea scallops	77-01	39	22	26	+	
Lobster	76-13	6	13	13	+	

pattern comparison on a firmer statistical basis, the reference cargo oil was processed through the entire analytical procedure for biota in quadruplicate. The 90% confidence intervals around the mean value of each alkane was established as an experimentally determined tolerance span (Figure 11).

The cargo reference patterns and associated tolerances produced by the two different procedures (Figures 10, 11) are similar but not identical. Consequently, minor differences occurred in the percentage of alkanes in the samples which fit the reference alkanes within the given tolerance. Comparisons of the percent fit by the "±⅓" and by the "90% confidence" criteria are listed in Table 1.

Despite differences of percent fit by the two criteria, the considerable similarities between the two data sets are reassuring. This supports the use of the ±⅓ tolerance as a simple way to approximate objective alkane pattern comparisons among samples suspected of being contaminated by spilled oil. On the other hand, if it is feasible to perform multiple analyses of the reference sample using the complete analytical procedure, the 90% confidence interval may provide a sounder tolerance criterion for pattern comparisons.

Two additional statistical operations were performed on the normalized alkane distributions from the biota vs. that of the cargo (Table 1). The first tested the medians of the biota and cargo data sets for differences using a chi-square test at the 90% confidence level. The second tested the diversity indices of the biota and cargo data sets for differences using t-test tables at the 90% confidence level. The medians and diversity indices of the relative abundance patterns for the stomach contents of:

(a) Cod: cruise 77-01, station 29,
(b) Cod: cruise 77-01, station 38, and
(c) Windowpane flounder: cruise 76-13, station 4

were not shown to be different than those of the *Argo Merchant* cargo (Table 1). These results are consistent with the highest percent fit values obtained by the two tolerance criteria which provide statistical support for visual comparisons of the gas chromatograms discussed above.

The use of the reference patterns in Figures 10 and 11 was based on the assumption of no differential weathering effects on the sample major alkanes. Since this could not always be expected to be the case, the ranking of sample major alkane patterns with respect to the reference was also calculated on the basis of the alkanes above n-$C_{16}H_{34}$ only (Figure 10) to allow for some of the more predictable effects of weathering (Clark and MacLeod, 1977). Interestingly, this allowance had little effect on the percent fit values for the alkanes from the biota or on their rank-ordering.

Of 36 sediment samples screened for evidence of *Argo Merchant* cargo by ultraviolet fluorescence (UVF) analysis by R. Jadamec of the U.S. Coast Guard (Grose and Mattson, 1977), 25 were forwarded frozen for GC and GC/MS analysis in our laboratory. Analysis of 10 sediment samples whose estimated contamination by the spilled oil exceeded 0.1 ppm by the UVF procedure (Grose and Mattson, 1977) failed to reveal any GC patterns or major hydrocarbon relative abundance patterns which could be readily related to the *Argo Merchant* reference cargo sample. The remainder of the sediment samples did not afford measurable levels of major alkanes or arenes by our procedure.

Summary

The saturated hydrocarbon fraction better demonstrated evidence of possible contamination from the *Argo Merchant* cargo than did the aromatic fraction. The best analytical evidence for cargo contamination was found in the gas chromatograms of the hydrocarbons from the stomach contents of two fish samples. The aromatic fraction afforded less evidence of contamination by the cargo oil than did the saturated fraction, primarily because the major cargo reference arenes failed to give measurable levels in most samples.

Acknowledgments

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A Comparison of Argo Merchant Oil and Sediment Hydrocarbons from Nantucket Shoals

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Abstract

Surface sediment samples collected from the Nantucket Shoals *Argo Merchant* wreck site area in February, 1977, were analyzed for hydrocarbon content by gas chromatography. Levels of hydrocarbons (n-C_{14} to n-C_{34} range) greater than 20 μg HC/gm dry weight sediment (ppm) were found at three stations, and traces of hydrocarbon contamination (0.7 to 1.1 ppm) were found at two other stations. Background levels in this area were less than 0.5 ppm. These findings indicate that significant hydrocarbon contamination extended at most 3-4 km from the wreck site in a SE direction. Traces of contamination were found 3-5 km from the wreck in the E and S directions. At the highly contaminated stations, the majority of hydrocarbons were in the form of minute tar particles mixed with sand. Analysis of sediment grab subsections revealed no clear trend of hydrocarbon contamination as a function of depth in sections as deep as 10 cm. Analyses of box core sections showed that contamination extended at least to 8-13 cm in depth. The stations which were found to contain significant hydrocarbon contamination in February were reoccupied on a cruise in July, 1977. Only the sediments at the bow section of the wreck site showed contamination (0.6 ppm) and these levels were significantly lower than found at this site in February (4 to 122 ppm).

The high degree of physical activity on the shoals is probably responsible for the areal patchiness and the inhomogeneous mixing of hydrocarbons with depth in the sediments. Although chemical, physical and biological weathering could be responsible for the observed decrease in hydrocarbon concentrations at the wreck site, turbulent mixing on the shoals probably transported the contaminated sediments out of the area or buried them under clean sand.

The chromatographically resolved hydrocarbon components of the tar particles and sediments were statistically compared with the resolved components of the *Argo Merchant* cargo oil. The hydrocarbons in the tar particles, and those sediments collected in February in the immediate vicinity of the wreck sites, matched well with the *Argo Merchant* cargo. The hydrocarbons in the sediments collected 3 km from the wreck in February and sediments collected at the wreck site in July match poorly with the cargo sample.

Introduction

On December 15, 1976, the tanker *Argo Merchant* ran aground on Fishing Rip of Nantucket Shoals off the Massachusetts coast. Within one week she had broken into three parts, the stern and midsection remaining aground near the original point of impact and the bow section floating and eventually sinking 2.8 km SE of the stern section. During these events, approximately 28 x 10^3 metric tons of No. 6 fuel oil were spilled into the ocean. In order to determine the degree to which the sediments were contaminated in the vicinity of the wreck site and Little Georges Bank, the University of Rhode Island organized five cruises to the area. On several of the earlier cruises which collected sediments over a 4000 km^2 grid, the U.S. Coast Guard conducted on-board hydrocarbon screening using UV fluorescence spectroscopy, the results of which indicated that the sediments were contaminated with *Argo Merchant* oil only around the wreck site (Grose and Mattson, 1977). On the basis of these findings, a detailed sediment survey of the wreck site area was conducted on R/V *Endeavor* cruise 005, February 22-27, 1977. Several of these stations were reoccupied in July 22-24, 1977, five months later, on F/V *Sideshow* cruise 001.

The objectives of this study were as follows: (1) determination of the areal extent of surface sediment contamination by the *Argo Merchant* oil; (2) measurement of the depth of sediment contamination; and

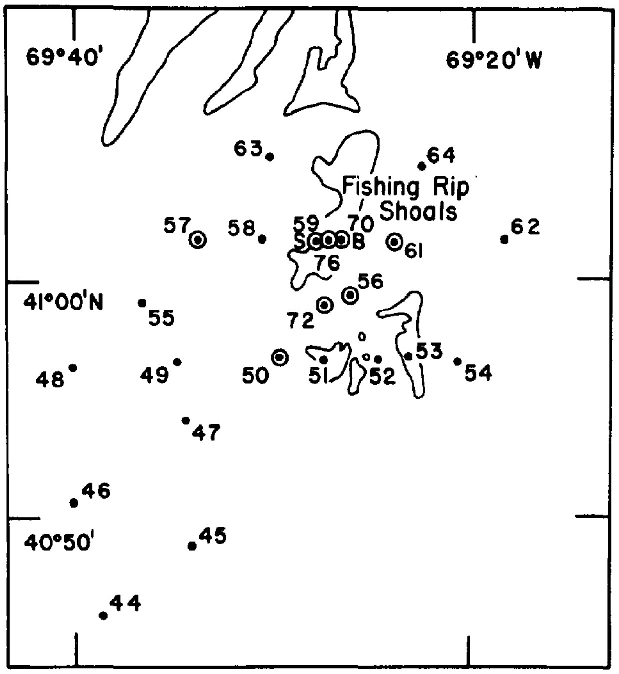

Figure 1. *Station locations of EN-005 (February 22-27, 1977), and SS-001 (July 2-24, 1977). The "S" (Station 59) is the location of the Argo Merchant stern and mid section wrecks and the "B" (Station 70) is the location of the Argo Merchant bow section. The circled dots are the stations from which the sediments analyzed in this study were collected. The other stations were analyzed by the U.S. Coast Guard.*

(3) evaluation of physical, chemical and/or biological weathering of the oil as a function of time.

Experimental Procedures

Sediment Sampling. Sediment samples were collected from the Nantucket Shoals *Argo Merchant* wreck site area aboard R/V *Endeavor* (EN-005, February 22-27, 1977) and aboard F/V *Sideshow* (SS-001, July 22-24, 1977) (Figure 1). Surface sediment samples (0-15 cm) were collected with a Smith-McIntyre grab sampler. One-half of each grab sample was preserved in formalin for biological archiving purposes. From the other half, used for chemical analysis, successive subsamples were placed into individual one quart Mason jars. The depths noted in the results section are estimates of the different depths in the grab sampler from which the individual subsamples were taken. After a small portion (5 cc) of each subsample was removed for on-board screening by Coast Guard personnel, the remainder of each subsample was frozen until later analysis (*Sideshow* sediment samples were stored in an ice locker while at sea and subsequently frozen upon return to the laboratory). Sediment cores (13-14 cm each) were obtained on EN-005 with a box corer. Three subsamples of each core were taken with plastic core liners. Two subsamples were used in benthic flux experiments. The third subsample, analyzed in this study, was frozen immediately after collection.

Cargo and Slick Sampling. One cargo sample and two surface slick samples were collected by Dr. Jerome Milgram of MIT who graciously provided subsamples of these for analysis and information on the collection and storage procedures (Milgram, personal communication, 1977). The *Argo Merchant* cargo oil sample was collected on December 19, 1976. The cargo sample, from the full port tank #4, was taken by putting a glass jar into the tank, withdrawing the jar and closing it. The first slick sample (Milgram #1) was collected on December 19, 1976, by lowering a bucket from the side of the USCGC *Vigilant.* The sample came from a distance of 2 to 4 km from the ship and Milgram estimates that it had been on the water for about one hour. The second sample (Milgram #2) was collected on December 25, 1976, at 40°54'N, 68°38.1'W, from a large pancake, also by lowering a bucket from the side of the USCGC *Vigilant.* It had probably been on the water for about four or five days. The cargo and slick samples were stored at room temperature in closed glass jars; after arrival in our lab, they were stored at 0°C until analyzed.

Sediment Analysis. Selected sediment samples from EN-005 were chosen for analysis on the basis of two criteria: (1) evidence of measurable or trace quantities of petroleum based on the Coast Guard screening results and/or (2) presence of minute tar particles which appeared on the top of the formalin surface of the biology subsample upon agitation of the sediment. Selection of SS-001 samples were based on (1) indications of contamination found on previous cruises and (2) stations adjacent to contaminated stations of earlier cruises. Occasionally minute tar particles (1 to 2 mm) were removed from the samples with tweezers prior to analysis, and the tar particles and sediment were analyzed separately.

After determination of the moisture content of a small portion of each sediment sample, 70-240 gms of wet sediment (50-200 gms dry weight) was weighed into a two ℓ round bottom flask. Generally 60 μg of n-C_{20} and 200 μg of n-C_{22} were added as internal standards for the EN-005 samples, and 20 μg of n-C_{20} and 100 μg of n-C_{22} were added as internal standards for the SS-001 samples. The samples were then saponified using 500-800 ml of a 70% 0.5 N KOH/methanol - 30% toluene mixture under reflux conditions for 2 hours. Enough water was added to the mixture (10 to 20% of the methanol) to prevent transesterification. The sediment-solvent mixture was allowed to cool and then filtered using a pre-ignited Whatman GF/C filter. The sediment and filter were washed with methanol, then with petroleum ether. The filtrate and combined washings were transferred to a two ℓ separatory funnel and separated into two phases by adding an amount of distilled water equal to the amount of methanol. The non-saponifiable fraction (petroleum ether-toluene phase) was separated from the saponifiable fraction (water-methanol phase) and the latter phase was extracted two additional times with petroleum ether. The petroleum ether extracts were combined and added to the non-saponifiable fraction and evaporated to dryness on a rotary evaporator at 35-40°C. The residue was charged to a column in one ml of a 95% petroleum ether-5% toluene mixture. This column, prepared in a Pasteur pipette, contained (from bottom to top) a glass wool plug, 0.3 gm Cu powder (activated with 3N HCl), 1 gm silica gel (deactivated with 5% water), 1 gm alumina

Table 1. Total hydrocarbons in selected sediment samples from Cruise EN-005. February 22-27, 1977.

Station (replicate)	*Latitude*	*Longitude*	*Depth of sediment (cm)*	*Total hydrocarbons μg/gm (dry wt sediment)*
50(1) G*	40° 57.1'N	69° 30.1'W	0-1	<0.1
50(2) G	40° 56.9'N	69° 29.9'W	0-1	0.8
50(2) G	"	"	1-3	0.4
50(2) G	"	"	3-5	<0.1
56(1) G	40° 59.2'N	69° 27.0'W	0-1	1.2
56(3) G	40° 59.2'N	69° 27.3'W	0-1	<0.3
56(4) G	40° 59.0'N	69° 29.0'W	0-1	21.5
57(1) G	41° 02.0'N	69° 33.5'W	0-1	<0.1
59(1) G	41° 02.5'N	69° 27.3'W	0-1	2.4†
59(1) G	"	"	1-3	0.5
59(1) G	"	"	3-5	<0.1†
59(3) G	41° 03.0'N	69° 27.5'W	0-1	2.6†
59(3) G	"	"	1-3	<0.1
59(3) G	"	"	3-5	<0.1
59(4) G	41° 02.9'N	69° 27.2'W	0-1	0.3
59(4) G	"	"	1-3	0.1
59(4) G	"	"	3-5	<0.1
59(1) BC**	41° 02.5'N	69° 27.0'W	0-3	5.1
59(1) BC	"	"	3-8	1.3
59(1) BC	"	"	8-13	24.6
59(2) BC	41° 02.6'N	69° 27.0'W	0-4	0.3
59(2) BC	"	"	4-9	0.8
59(2) BC	"	"	9-14	0.4
61(2) G	41° 02.6'N	69° 22.5'W	0-1	1.1
61(3) G	41° 01.0'N	69° 23.0'W	0-1	0.7
70(1) G	41° 01.8'N	69° 26.2'W	0-1	12.8
70(1) G	"	"	1-3	29.6
70(1) G	"	"	3-5	11.5
70(1) G	"	"	>5	19.7
70(3) G	41° 02.0'N	69° 26.6'W	0-1	10.2
70(3) G	"	"	1-3	4.0
70(3) G	"	"	3-5	5.6†
70(4) G	41° 02.0'N	69° 26.5'W	0-1	118, 69.7, 35.7††
70(4) G	"	"	1-3	5.1
70(4) G	"	"	3-5	122
70(1) BC	41° 02.0'N	69° 26.5'W	0-3	1.9
70(1) BC	"	"	3-8	2.7
70(1) BC	"	"	8-13	2.2
70(2) BC	41° 01.9'N	69° 26.3'W	0-3	2.7
70(2) BC	"	"	3-8	28.2
70(2) BC	"	"	8-13	37.5

**G = Smith-McIntyre grab samples*
† tarball removed prior to analysis
*** BC = box core samples*
†† triplicate analysis

(deactivated with 5% water), and another glass wool plug. The sample was eluted with 15 ml of the 95% petroleum ether-5% toluene mixture. It was found that this column procedure retained elemental sulfur, methyl esters, methyl ketones and more polar organic compounds while eluting hydrocarbons including *n*-alkanes, and aromatics, such as phenanthrene, pyrene and chrysene. The petroleum ether-toluene mixture was then evaporated to dryness and dissolved in methylene chloride. Each sample was analyzed by gas-liquid chromatography (GLC) with a Hewlett-Packard Model 5711A or 5840A gas chromatograph equipped with dual flame ionization detectors. Most of the analyses were accomplished using dual packed columns (2m, 2.2 mm i.d. stainless steel) containing 10% SP-1000 on Supelcoport, 80/100 mesh. A few analyses were done using a glass capillary column (15 m, 0.25 mm i.d., OV-101, Quadrex Corp.). The hydrocarbons measured eluted from the column between n-C_{14} and n-C_{34} using temperature programming from 90°C to 260°C at 8°/minute for the packed column and 60°C to 240°C at 4°/minute for the capillary column. The chromatograms were quantified by comparing the areas of the chromatograms with the areas of the n-C_{20} and/or n-C_{22} internal standards.

Procedural blanks were determined by carrying solvents and internal standards through the analysis procedure in the absence of the sediments. The average blank was 23 ± 10 μg/sample. Concentrations were reported for all sediment samples in which the blank correction represented <50% of the blank plus sample value. For a 200 gm sediment sample, this would yield a detection limit of approximately 0.1 ppm (23 μg/200 gm). Whenever the blank correction was greater than 50% of the total, the values were reported as less than the detection limit for that specific sediment sample weight. All the values reported in the tables have been corrected for the blank.

Cargo, Slick, and Tar Particle Analysis. After weighing, these samples were dissolved in the 95% petroleum ether-5% toluene mixture and charged to the Cu-silica gel-alumina column described previously. The hydrocarbon elutant was evaporated to dryness, dissolved in methylene chloride, and analyzed by GLC.

Results and Discussion

A. Areal Extent of Sediment Contamination. The locations where sediment was collected on EN-005 are given in Figure 1. Sediments from all of these stations were prescreened by Coast Guard personnel. This study presents detailed GLC analysis only on those samples found to have at least some trace of oil by the Coast Guard technique or those samples from which small tar particles floated out of the corresponding biological samples. A total of 45 subsamples from six EN-005 stations and 15 subsamples from six SS-001 stations were analyzed. These latter stations are also shown in Figure 1.

The present data (Table 1) indicate that in February, 1977, the sediments were significantly contaminated at 3 stations (56, 59, 70 - significantly defined as greater than 20 μg HC/gm dry weight, a value ranging from 40 to >200 times higher than the background hydrocarbon concentrations). Two of these stations were located at the wreck site locations: Station 59 at the original wreck site (now the location of the mid and stern sections); and Station 70, the location of the bow section. Station 56 is located 3.2 km SE of the bow section in the channel adjacent to Fishing Rip Shoal. The sediment at 59 and 70 was coarse sand while the sediment at 56 was gravel mixed with crushed shells and mud. Background hydrocarbon levels in the area were less than 0.5 μg/gm. Trace levels of petroleum (0.7 to 1.1 μg/gm) were found at Stations 50 and 61. (Station 50 was 4.8 km SW of the wreck; Station 61 was 3.2 km E of the wreck.) Both of these stations were located in the channel to the S and E of the wreck and the presence of traces of petroleum hydrocarbons at these locations could either be from sources other than the *Argo Merchant*, or from the *Argo Merchant* itself. Since the Coast Guard found no evidence of *Argo Merchant* oil at the other stations and, assuming that their results are correct, our findings would indicate that significant sediment contamination in February extended at most 3-4 km from the wreck site in a SE direction. Traces of contamination from an unknown source could be found 3-5 km from the bow in the E and SW directions. At most, this would indicate that in February, a 10-15 km^2 area of the sediments were contaminated. It is likely that only a small percentage of this area was significantly contaminated, these areas being limited primarily to the immediate vicinity of the wreck site, especially around the bow section.

B. Depth of Contamination. An attempt was made to determine the depth of sediment contamination by taking successive subsamples out of Smith-McIntyre grab samples or by examination of box cores. Neither sampling device collected sand any deeper than 13-20 cm, and in the case of gravel bottom stations, a maximum of only 3-4 cm of sediment was collected. No clear trend as a function of depth was noted in the EN-005 sediment samples. For example, at Stations 70(1)BC and 70(1)G, the hydrocarbon concentrations were fairly constant with depth, while at Stations 59(1)BC, 70(4)G, and 70(2)BC, the higher concentrations generally appear in the subsurface sediments, and at Stations 59(1)G and 59(3)G the highest concentrations appear in the surface sediments (Table 1). The probable reasons for this variation are: patchiness due to inhomogeneous mixing of minute tar particles into the sand, coupled with the highly active physical nature of the shoals. The tidal currents in this area at times exceed 3 knots. Such current speeds will result in erosion and transportation of coarse sand as found on the shoals and then deposition elsewhere as the current slackens (Heezen and Hollister, 1964). Then the tidal current reverses direction and the process occurs again, this time in an opposite direction. The depth to which this erosion-deposition cycle extends with each half tidal cycle has not been studied on Nantucket Shoals but has been shown to involve at least 2 meters on Middle Ground (a shoal in Vineyard Sound, Massachusetts), and at times sediments as deep as 6 meters can be moved (Smith, 1969). In this present study, it can only be concluded that contamination of some of the sediment extends at least to 8-13 cm in depth. Clearly, the possibility exists that the contamination could be significantly deeper than this.

C. Nature of Sediment Contamination. It was found that at least some of the petroleum hydrocarbons in the sediments were associated with minute tar particles. In order

Table 2. Comparison of total sediment hydrocarbon concentrations with and without inclusion of tar particles (EN-005 sediments).

Stat/Rep/Depth*	*Total hydrocarbons μg/gm (dry wt sediment)* Sediment with tar particles physically removed	Tar contribution	Sediment with tar particle contributions included
59(1)0-1	2.4	73.5	75.9
59(1)3-5	<0.1	48.5	48.6
59(3)0-1	2.6	324	327
70(3)3-5	5.6	29.1	34.7

all grab samples, depth in cm

to find out the approximate percentage of the total hydrocarbons these tar particles represented, particles were physically isolated with spatula and tweezers from four of the samples. The sediments (without their tar particles) and the tar particles were analyzed separately. The result of this experiment is given in Table 2. In all cases, the tar particle contribution to the sediments was the major contribution rather than any coating on the sand. It is also clear that the number and size of the tar particles in any one sediment sample is going to greatly affect the results. In order to minimize this problem, large sediment weights (usually 100 to ~ 200 gms) were used for each analysis in this study. In spite of this precaution, replicate analyses from the same subsample indicate variabilities of a factor of three. (See Station 70(4)0-1 in Table 1 for replicate analyses data.) Since the uncertainty for the analytical procedure is no greater than 10%, the sediment samples were inhomogeneous even when taken from the same storage container. This is undoubtedly one of the reasons, perhaps the major one, why the Coast Guard on-board screening analytical results do not agree in all cases with the results presented here. Although our values are generally lower, there is some correlation between the Coast Guard screening analysis and our analysis ($r = 0.69$ for 20 samples) in spite of the patchiness. The patchiness due to inhomogeneous mixing of the tar particles into the sand as a result of the physical activity of the area led to even greater variations from grab sample to grab sample even within 50 meters of each other. At Station 70, for example, the upper sediments (0-3 cm depth) in replicate grab and core samples contained 12.8, 10.2, 118, 1.9 and 2.7 μg/gm, a variation over two orders of magnitude. Thus the observed patchiness exists both on micro as well as a macro scale.

D. Comparison of Slick, Sediment and Tar Particle Samples with the Argo Merchant Cargo Oil. The chromatographically resolved portion of the hydrocarbon components of the tar particles, sediments and slick samples were compared with the resolved components of the *Argo Merchant* cargo oil, by a simple technique of comparing areas of each resolved component. It should be pointed out that the *Argo Merchant* carried two cargos, both No. 6 fuel oils, but only one of the cargos was sampled at the scene. It was this cargo sample that was used for matching purposes in this study. Although these oils were reported to be nearly identical (Grose and Mattson, 1977), some of the following matching experiments could have been affected by differences in the

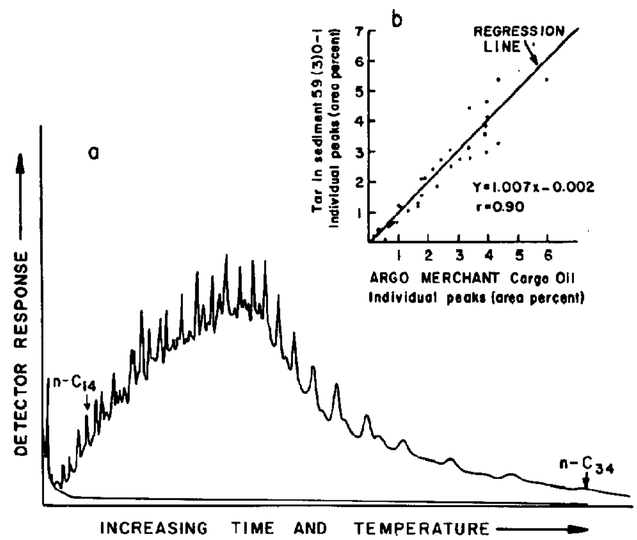

Figure 2. *Part A. Chromatogram (packed column) of tar particles separated from the sediment collected at Station 59, Grab 3, 0-1 cm depth, in February 1977. Part B. Graph of the areas of each resolved hydrocarbon component of this tar particle sample versus the area of the corresponding peaks in the Argo Merchant cargo.*

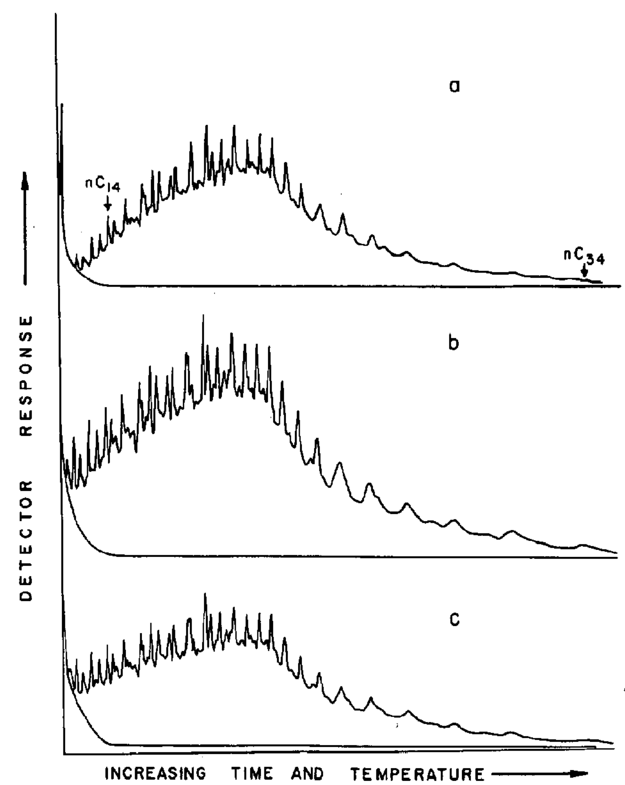

Figure 3. *Part A. Chromatogram (packed column) of the Argo Merchant cargo oil. Part B. Chromatogram (packed column) of a surface slick sample (Milgram #1) collected on December 19, 1976. Part C. Chromatogram (packed column) of a surface slick sample (Milgram #2) collected on December 25, 1976.*

Table 3. Comparison of resolved components in slick, sediment and tar particle samples with *Argo Merchant* cargo oil sample.

y	*y vs. Argo Merchant correlation coefficient*	*No. of area %'s*	*sig. level*
Argo Merchant duplicate analyses same day	0.99	31	>0.995
Argo Merchant duplicate analyses 2 days apart	0.97	38	>0.995
Argo Merchant duplicate analyses — same day	0.93*	17	>0.995
Oil sample on water one day (Milgram #1)	0.91	38	>0.995
Oil sample on water five days (Milgram #2)	0.96	39	>0.995
Tar — station 59 (1) 0-1 (EN-005)	0.89	24	>0.995
Tar — station 59 (1) 3-5 (EN-005)	0.79*	17	>0.995
Tar — station 59 (3) 0-1 (EN-005)	0.90	40	>0.995
Tar — station 70 (3) 3-5 (EN-005)	0.44	25	0.975
Sediment and tar station 70 (4) 3-5 (EN-005)	0.98	39	>0.995
Sediment without tar station 70 (3) 3-5 (EN-005)	0.74	27	>0.995
Sediment — station 59 (1) BC 8-13 (EN-005)	0.86	19	>0.995
Sediment — station 56 (4) 0-1 (EN-005)	0.21*	13	<0.95
Sediment — station 70 (1) 0-1 (SS-001)	0.18*	14	<0.95

**glass capillary major peaks*

resolved component pattern between the two cargos.

With the help of the HP-5840 integrator, the area of each peak (or resolved component) was expressed in area percent as per Equation (1):

$$A\%_i = \frac{A_i}{\Sigma A_i} \times 100\%$$

where $A\%_i$ is the area % of the individual resolved component, and A_i is the area in arbitrary units of each individual peak. The individual area percents of each peak of the standard (in this case, the *Argo Merchant* cargo oil sample collected by J. Milgram) are then plotted versus the corresponding area percents (using peaks having the same retention times) of the sample. All the reported peaks were used in the case of packed column chromatograms; however, only the major peaks (with area percentages greater than 1%) were included when glass capillary GLC was used. An example of the result is given in Figure 2. The area percents of each resolved peak in the chromatogram (Part A of Figure 2) were plotted versus the corresponding peaks in the cargo sample (Part A of Figure 3) to yield the resulting graph given in Part B, Figure 2. Visually the chromatograms look similar and linear least squares regression analysis of the individual area percents confirms a strong correlation (r = 0.90). An example of a poorer match is given in Figure 4. Here the resolved pattern of the sample visually does not look like the cargo sample. The peaks are less pronounced and in some places are absent altogether. Again the linear least squares regression analysis of the area percents of the resolved species indicates a poor correlation (r = 0.44). A summary of these examples and other samples compared to the *Argo Merchant* cargo is given in Table 3. Occasionally, a glass capillary column was used for the matching experiments. An example of the *Argo Merchant* oil chromatogram using glass capillary gas chromatography is given in Figure 5, part A.

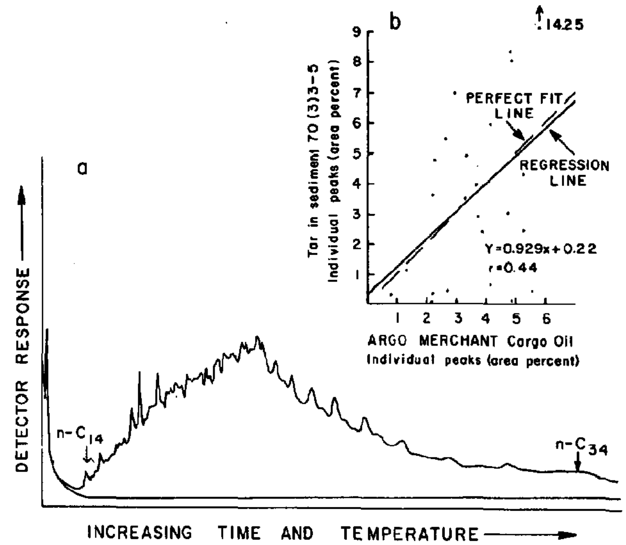

Figure 4. *Part A. Chromatogram (packed column) of tar particles separated from the sediment collected at Station 70, Grab 3, 3-5 cm depth, in February, 1977. Part B. Graph of the areas of each resolved hydrocarbon component of this tar particle sample versus the area of the corresponding peaks in the Argo Merchant cargo.*

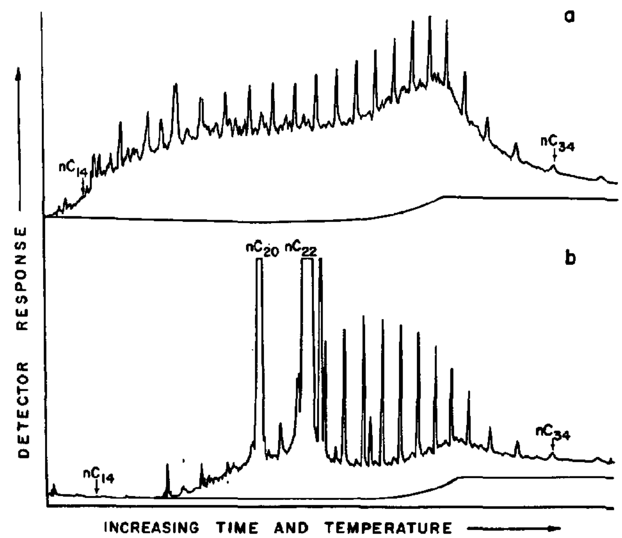

Figure 5. *Part A. Chromatogram (glass capillary column) of the Argo Merchant cargo oil. Part B. Chromatogram (glass capillary column) of the sediment collected at Station 70(1), 0-1 cm depth, in July, 1977. (The n-C_{20} and n-C_{22} are internal standards added for quantitation purposes.)*

In order to demonstrate the correlations obtained using duplicate injections, *Argo Merchant* cargo oil was analyzed using different injection conditions (as noted on Table 3). All of these procedures yielded strong correlations ($r > 0.90$) for *Argo Merchant* oil versus *Argo Merchant* oil. The chromatograms of the cargo and surface slick oil samples are given in Figure 3. Visually there is a strong resemblance and the correlations of the resolved area percents also confirms this strong correlation (Table 3). There is little evidence of weathering in slick samples up to 5 days. This is particularly interesting, since the *Argo Merchant* cargo contained about 20% of a cutter stock of light oil added to the No. 6 oil (Grose and Mattson, 1977). Apparently, there had not been substantial losses of these lighter components during the 5 days it was on the surface of the water. Undoubtedly the cold atmospheric temperature impeded the evaporative losses. (The mean temperature for these 5 days was -3°C, National Weather Service, Warwick, R.I.) In addition, the cold weather may have reduced the dissolution of the more potentially soluble components from the slick into the water column.

Three of the four tar particle samples also match well with the cargo oil ($r = 0.79$ to 0.90, Table 3). The other tar particle sample (sample 70 (3) 3-5, also shown in Figure 4), apparently had undergone some weathering, or was from a different source. The sediments collected around the wreck site matched well with the cargo although the sediment with the visible tar particles removed did not match as well as the other sediments from the wreck site. The hydrocarbons in the sediments collected 3 km from the wreck site in February (Station 56 (4)0-1, EN-005) did not match with the cargo oil; the chromatogram showed that either extensive weathering of the resolved peaks had taken place (if the hydrocarbons were *Argo Merchant* derived), or the hydrocarbons at this station were a weathered product of some other petroleum input. The hydrocarbons found in the sediments in July (Station 70 (1), SS-001) also did not match with *Argo Merchant* oil and the glass capillary chromatogram of these hydrocarbons is given in Figure 5, Part B. Visually there is little similarity between the resolved hydrocarbon pattern of the *Argo Merchant* cargo and this July sample. The July sediment pattern does, however, resemble patterns of tar lumps found on Bermuda beaches reported by Butler et al. (1973), patterns of tar particles >1 cm diameter in size in the N. Atlantic reported by Wade et al. (1976), and patterns for hydrocarbons in surface microlayers in coastal waters south of Martha's Vineyard in February, 1977 (Boehm, 1977). It can therefore only be concluded that the source of the hydrocarbons in the vicinity of the *Argo Merchant* wreck site in July is unknown. Clearly more information concerning the source of the hydrocarbons found in these environmental samples where poor matches were obtained could be learned if specific persistent compounds unique to the cargo could be found and studied in the samples.

E. Variation with Time. On July 22-24, 1977, five months after the R/V *Endeavor* cruise 005 in February, and seven months after the initial spill, further sediment samples from the wreck site areas were collected aboard F/V *Sideshow.* Samples were collected for chemical analysis and biological archiving at all the previously contaminated stations found on EN-005, with the exception of Stations 56 and 57 (where the July samples contained only cobbles and shell fragments). The hydrocarbon analytical results are given in Table 4. The samples all contained 0.6 μg HC/gm or less. Only at one station (Station 70 (1)) were traces of petroleum hydrocarbons found. An example of the chromatograms for this station is given in Figure 5B. Note that the chromatogram does not compare well with the *Argo Merchant* oil cargo chromatogram (Figure 5A), and there is no statistical correlation for the resolved components ($r = 0.18$,

Table 4. Total hydrocarbons in selected sediment samples from Cruise SS-001. July 22-24, 1977.

*Station * (replicate)*	*Latitude*	*Longitude*	*Depth of sediment (cm)*	*Total hydrocarbons µg/gm (dry wt sediment)*
50 (2)	40° 56.9'N	69° 30.1'W	0-1	0.1
59 (1)	41° 02.5'N	69° 27.8'W	0-1	0.2
59 (2)	"	"	0-1	<0.1
59 (3)	"	"	0-1	<0.2
61 (1)	41° 01.5'N	69° 24.3'W	0-1	0.4
70 (1)	41° 02.0'N	69° 26.8'W	0-1	0.5
70 (1)	"	"	1-3	0.6
70 (1)	"	"	3-5	0.6
70 (1)	"	"	5-10	0.4
70 (2)	41° 02.0'N	69° 26.8'W	0-1	0.2
70 (3)	41° 02.0'N	69° 26.8'W	0-1	<0.2
72 (2)	40° 59.2'W	69° 27.7'W	0-1	0.2
76 (1)	41° 02.0'N	69° 26.5'W	0-1	0.2
76 (2)	41° 02.4'N	69° 26.8'W	0-1	<0.2
76 (3)	41° 02.7'N	69° 27.7'W	0-1	0.4

**all grab samples*

Table 3). Since this sediment sample was collected at the *Argo Merchant* bow section wreck site station, it is tempting but highly unlikely to conclude that this is *Argo Merchant* oil after 7 months of physical and chemical weathering and/or biological degradation. This is unlikely since the *n*-alkanes which appear predominantly in the sample are usually the first to degrade with time relative to the complex mixture of cycloparaffins, aromatics and naphtheno-aromatics. These hydrocarbons could have been from non-cargo sources of oil from the *Argo Merchant* (i.e. hydraulic fluids, etc.) or from non-*Argo Merchant* sources altogether. With the exception of this station (Station 70(1)), the rest of the samples gave no evidence of petroleum hydrocarbons, weathered or otherwise, above the normal background levels.

Since the fishing vessel had a draft of only 2 meters, it was possible to collect sediment samples on top of the shoal, between the bow and stern section locations, a feat not possible with R/V *Endeavor* (draft of over 5 meters). Stations 76(1), 76(2), and 76(3) represent a transect across the shoal from the bow site to the stern site. It was felt that sediments at these stations might have been heavily contaminated with oil as the bow section drifted over them before it was sunk (Grose and Mattson, 1977). In July, no evidence of such contamination was found. Again because of the turbulence of the area, the oil could have been degraded, buried or transported away from the shoal, especially since seven months had passed from the time of the original spill.

No evidence of either transportation to other adjacent stations (50, 61, 72) or burial at the wreck site was found. Again, since we obtained sediments only as deep as 10 cm, it is unwarranted to make conclusions based on such samples when daily fluctuations in sediments of two meters are possible.

In summary, the hydrocarbon concentrations in the surface sediments in the vicinity of the *Argo Merchant* wreck site in July, 1977, were significantly lower than found on the earlier cruise in February. At only one station was evidence of petroleum hydrocarbon contamination found, and these hydrocarbons did not match the *Argo Merchant* cargo oil.

F. Mass Balance Considerations. A rough estimate of the percentage of spilled oil which became incorporated in the sediments can be made if a series of assumptions are used. Generally these assumptions tend to maximize the amount of oil in the sediments: (1) Assume an average concentration of hydrocarbons in the vicinity of the wreck (Stations 59 and 70) in February, 1977, is 16 ppm (arithmetic mean ± the standard deviation was 16 ± 30 ppm); (2) Assume a linear rate of weathering or dispersal with time, such that 16 ppm in February decreased to an average of 0.3 ppm in July in a linear decrease (extrapolation of this date back to December, 1976, produces an average minimum value hydrocarbon concentration of 22 ppm); (3) Assume an affected area of 15 km^2; (4) Assume a depth of contamination of 15 cm, and a constant concentration of hydrocarbons with depth; and (5) The average sediment density is approximately 3 gm/cm^3. Using these assumptions, it was calculated that a maximum of 1.5×10^2 metric tons of oil was incorporated in the sediments, or 0.5% of the total oil spilled. It is felt that this amount represents a maximum estimate. This calculation would therefore indicate that surface sediments in the vicinity of the wreck site were not a major sink for the oil in the case of the *Argo Merchant* oil spill.

Acknowledgments

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We also thank EPA-Narragansett for the use of the Smith-McIntyre grab samplers.

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Biological Studies

Kenneth Sherman, Chairman

Summary of Biological Studies

The discussions of biological effects of *Argo* oil on marine populations were wide ranging and not as sharply focused as the physical and chemical sessions. Prior to the *Argo* spill no large-scale effort to assess oil-related biological damage had been undertaken in the open waters of the continental shelf off the northeast coast. The concerns expressed by the Symposium participants emphasized the difficulties in attributing changes in the abundance and condition of marine populations to oil as compared to changes from other causes. Attempts made to isolate oil induced mortalities or sublethal effects need to be viewed against the background of natural fluctuations and the complexities of multispecies interactions at different trophic levels and over a range of spatial and temporal scales. Studies to deal with these problems need to be in place and operational long before any acute spill event.

The results brought together at the Symposium, although somewhat fragmentary, were sufficient to indicate that the impact of *Argo* oil on the populations of Nantucket Shoals was minimal based on the short-term assessment studies carried out during the previous 12 months. Supporting evidence for this conclusion was found in both the population studies and the physiological effects studies done at the tissue and organism levels for molluscs, fish, birds, zooplankton, and benthic crustaceans. In the histopathological, biochemical, and physiological studies the recovery from initial observations of sublethal impact to "normal" conditions was reported for each of the groups of organisms examined, except for marine birds. The bird mortalities caused by oil, however, were few and the impact on bird stocks was not considered significant. Genetic damage was observed in developing cod and pollock embryos, but the effect was localized and it is unlikely to have a significant effect on subsequent year-class recruitment of these stocks. Results of laboratory petroleum hydrocarbon exposure studies of developing cod embryos indicated that concentrations of 250 ppb were lethal. Although this level of oil was detected, the area of concentration was limited to the immediate vicinity of the *Argo* wreck, and is likely to have affected a relatively small fraction of the Nantucket Shoals cod stocks.

Trophic pathways of *Argo* oil were observed among the zooplankton and benthos leading directly to important fish stocks. Further comprehensive stomach analyses of fish revealed a minor incidence of "oiled" prey in the digestive tracts of fish. Less than five percent of the fish examined showed any traces of *Argo* oil in tissue samples collected within 30 days of the spill. On subsequent surveys of bottom fish no *Argo* oil traces were found in fish, shellfish, or zooplankton samples. Commercial catches and bottom trawl surveys of the spill zone and adjacent areas showed no evidence of reduction in the population densities of the more important fish and shellfish stocks.

The limited short-term impact was attributed to the mitigating ecological circumstances during the spill: 1) biological productivity was at an annual low, 2) no large scale deposition of oil was observed in the sediments, and 3) the high velocity wind and currents of the season carried the oil, limited in its distribution largely to the surface, rapidly offshore while it was in the process of evaporation, emulsification, and dissipation in the turbulent upper layers of the water column.

The longer term ecological effects will be more difficult to assess against the background of natural fluctuations in population abundance. Time-series observations in the spill area are continuing jointly by the Northeast Fisheries Center of the National Marine Fisheries Service and the Manomet Bird Observatory. Damage assessment of acute spills of oil and other potential toxicants needs to be considered against baselines of population densities and their physiological condition. The existing baseline for marine populations off the east coast requires some augmentation, particularly with respect to "physiological effects" and "probable onshore effects." In addition, to ensure adequate scientific response to acute spills, an organizational matrix is required that considers national, regional, and local expertise of scientists and managers in the development of regional and local response plans.

Several specific recommendations for dealing with acute spill events on the continental shelf were made during the biological workshop session:

1. New methods and systems need to be developed for combining laboratory, *in situ* experiments, and populations assessment studies, in order to reduce the biases involved in extrapolations from small sample sizes to population level inferences.
2. A significant series of as yet unanalyzed biological samples and/or data pertinent to long-term studies is available particularly for benthos. Effort should be undertaken to support the completion of these studies.
3. More consideration should be given in the future to observations of primary production; this principal ecosystem component was not adequately examined in the *Argo* spill assessment.
4. Future biological studies should make greater use of risk-analyses projections in the planning and conducting of population assessments and laboratory studies of acute spills.
5. Concern was expressed over: 1) the persistence of tar clumps in the surface waters and their effects on biological populations; and 2) the persistent municipal and industrial input of petroleum hydrocarbons and other

toxic substances and their effects on the marine ecosystem. Additional research effort in the Northeast should be directed to deal with these problems.

6. The need was expressed, and a recommendation endorsed by the participants, for developing national standards for acceptable levels of petroleum hydrocarbons in fish and shellfish.

Considerable effort is now underway in the Northeast by NOAA and EPA to develop a regional response plan that will be implemented in the event of a large-scale spill of oil or other toxic substances, as a direct result of the *Argo Merchant* incident. Although our knowledge of the effects of petroleum hydrocarbons on marine populations of the outer continental shelf remains rather incomplete, the *Argo* incident is serving as a catalyst to overcome existing deficiencies.

Kenneth Sherman, Chairman
Biological Studies Session

Microscopic Observations on Vertebrates and Invertebrates Collected Near the *Argo Merchant* Oil Spill

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Abstract

Fish, molluscs, crustaceans, sea urchins, and starfish were collected from control stations and from stations which were selected because of their proximity to the *Argo Merchant* oil spill. Histopathological findings that could be attributed solely to exposure to petroleum were not seen in any of the tissues examined. Although collections probably were made too soon after the oil spill for potential tissue damage to have occurred, the microscopic findings provide baseline data for future studies. Several fish species had edematous gills, detached epithelium, or hyperplasia of the olfactory epithelium. Molluscs, sea urchins, and starfish tissues were unremarkable. Hermit crabs had sessile ciliate protozoa attached to the antennae and numerous granulocytic hemocytes in the hemolymph. Additional studies on hemolymph of hermit crabs are necessary to determine whether abundant granulocytes are characteristic of this host.

Early in 1977 the Pathobiology Investigation staff of the Oxford Laboratory was asked to participate in a multi-disciplined study of the marine organisms that might have been affected by the *Argo Merchant* oil spill. It was realized from the outset that the spill was too recent to assure that any observed pathology could be related directly to oil. However, it was thought that the study would provide an opportunity to obtain background information for future follow-up studies. The following report summarizes observations that were made on a diverse group of vertebrate and invertebrate species.

Methods

All animals were collected with an otter trawl, sorted, and preserved in neutral formalin. Specimens were identified, dissected for histological processing, and embedded in paraffin blocks. Sections were cut at 6 μm and stained with Harris's hematoxylin-eosin solutions or by the Feulgen-reaction. Stained sections were examined with routine bright-field microscopic procedures and photographed with Kodak Plus-X film. Specimens taken from control stations and oil-spill stations were compared to determine whether pathological conditions were present that could be attributed to petroleum hydrocarbon exposure.

Results

Fish, molluscs, crustaceans, sea urchins, and starfish that were processed for histological study are summarized in Tables 1 and 2. Molluscs were remarkably free of tissue pathology of any kind. Several fish (alewives, winter flounder) had edematous gills and detached epithelium, and the olfactory epithelium of yellowtail flounder appeared to be hyperplastic in areas of non-sensory and indifferent epithelium. *Ammodytes* larvae had ocular lesions and malformations or lack of pigmentation of the eye. None of the conditions observed in fish could be attributed directly to the effects of spilled oil.

Sea urchins and starfish did not have obvious signs of pathology or stress and all specimens examined appeared normal. Probable ciliate protozoa that were poorly fixed and stained in histologic sections were noted in the digestive tracts of several sea urchins. Live material was not available for study. One of the lobsters had several cellular nodules in the gill, pyknotic nuclei, and an encysted larval trematode. Hermit crabs had ciliates (sessile suctorians and loricate forms) attached to their

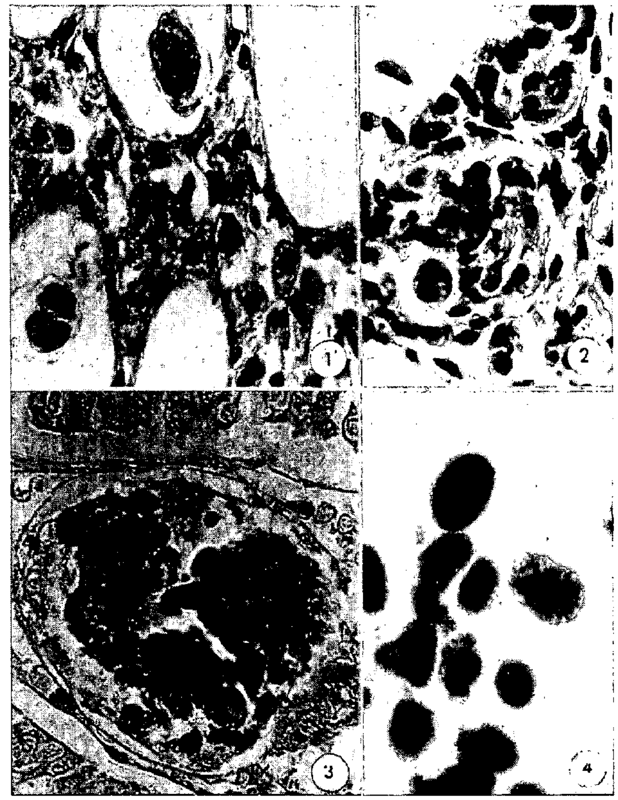
Table 1. Summary of species of fish and molluscs examined for histopathology.

Species	*Control Station*	*Oil Station*
	FISH	
Winter Flounder,	15	1
Pseudopleuronectes americanus	15	12
Yellowtail Flounder, *Limanda ferruginea*	15	7
Ammodytes sp. (larvae)	–	6
Totals	30	25
	MOLLUSCS	
Scallop, *Placopectin magellanicus*	15	25
Squid, *Illex illecebrosa*	1	–
Squid, *Loligo* sp.	1	8
Whelk, *Buccinum* sp.	–	5
Clam, *Artica islandica*	–	1
Clam, *Mytilus edulis*	–	1
Totals	17	40

Table 2. Summary of species of crustaceans, sea urchins, and starfish examined for histopathology.

Species	*Control Station*	*Oil Station*
	CRUSTACEANS	
Hermit Crabs, *Pagurus pollicaris*	6	12
Rock Crabs, *Cancer irroratus*	–	4
Lobsters, *Homarus americanus*	–	2
Totals	6	18
	SEA URCHINS	
Strongylocentrotus droehbachiensis (?)	–	9
Totals	–	9
	STARFISH[1]	
Asteria forbsei	2	5
Totals	2	5

[1]Starfish total includes one *Henricia* sp. (?) from an oil station.



Figures 1-4. *Photomicrographs of stained sections of various tissues of the hermit crab, Pagurus pollicaris. 1. Loricate sessile ciliates on gill cuticle. Harris hematoxylin-eosin, 640 x 2. Cellular response in eyestalk, note black degenerate nuclei. Harris hematoxylin-eosin, 640 x 3. Focal area of cellular degeneration localized in sinus of the hepatopancreas. Feulgen-reaction, 640 x 4. Large eosinophilic hemocytes in gill filament. Harris hematoxylin-eosin, 1600 x.*

gills or antennae (Figure 1); foci of tissue necrosis in the intestine, stomach, or eye stalk (Figure 2); necrotic areas in the hepatopancreas (Figure 3); and abundant granulocytic hemocytes (Figure 4). Although the hermit crabs had the greatest variety of tissue abnormalities, there were no specific differences in animals from the various collection sites.

Discussion

None of the microscopic findings from animals collected during the oil spill cruises could be related to the presence or absence of petroleum hydrocarbons. Abnormalities in fish and hermit crabs were remarkable and provided indications of the types of conditions that would be worthy of follow-up studies on long-term effects of oiled ocean-sediments. Specific effects of oil on wild-caught fish are difficult to measure because migratory habits may prevent associations from being made between control and stressed collecting stations. Bottom-dwelling crustaceans such as the hermit crab may be suitable since they are non-swimming animals and probably do not routinely move great distances. Similarly, starfish and sea urchins may be suitable for long-term studies on bottom-dwelling animals. The numbers of starfish and sea urchins were too small to be of value in the present study and their duration of exposure to oil probably was too short to initiate any detectable tissue response. Preliminary findings with hermit crabs indicated that they may have remarkably large numbers of granular hemocytes. Follow-up studies to determine whether or not exposure to oil has a rapid effect on crustacean hemocytes may prove useful for assessing some of the immediate effects of spilled oil on marine invertebrate species. Our studies show that in general, new information on the normal histology of fish, molluscs, crustaceans, etc., is essential to a better understanding of their subtle changes in response to environmental pollutants.

Considerations for Future Research

Stalked ciliates on the antennae and gills of hermit crabs collected in control and oil-spill stations provided indirect evidence that the full impact of potential harm caused by petroleum had not occurred at the time of the study. Sessile ciliate protozoans are known to reproduce by budding and shedding free-swimming ciliated larvae. The larvae in turn become attached to new substrates where they develop to the stalked adult stage. Langlois (1975) studied the effects of dissolved organic matter, phenols, and carbohydrates on substrate selection by motile telotroch larvae of *Vorticella marina* and found that certain algal exudates exert a significant influence on the distribution and settlement of *Vorticella* on aquatic substrates. New studies on the effects of oiled crustacean exoskeletons on settling rates of larval ciliates could be useful for investigating the fate and effects of oil in the environment. Jones and Rogers (1968) listed 7 species of ciliate protozoa from the intestinal tracts of 4 species of American sea urchins, and Beers (1961) discussed the adaptation of *Euplotes balteatus* to commensal life in *Strongylocentrotus droehbachiensis.* Recent studies by Andrews and Floodgate (1974) showed that free-living ciliates such as *Euplotes* and *Uronema* ingested oil residues while feeding on bacteria adhering to partially degraded oil globules. Published studies on sea urchins and ciliates suggest that benthic animals might ingest oiled food organisms with subsequent uptake of the oil by intestinal protozoa. The limited observations on sessile and endocommensal ciliate protozoa that were made in the present study indicate that they deserve further investigations under careful and well-planned field and laboratory conditions.

The effect of spilled oil on mortalities among benthic animal species is difficult to assess at sea. In contrast, it was estimated that 85 percent of the marketable clams, *Mya arenaria,* were killed following an oil spill in Long Cove, Searsport, Maine (Dow and Hurst, 1975). Nevertheless, it should be possible to study the population dynamics of certain animal species indigenous to shoals and ridges in the vicinity of known deepwater oil spill locations. Barry and Yevitch (1975) discovered a high incidence of gonadal tumors in *Mya arenaria* that were contaminated by the Long Cove oil spill. They continued their sampling program subsequent to the spill and found a 9 - 18 percent incidence of tumors 3½ years later.

It is apparent that our efforts to respond to the *Argo Merchant* oil spill suffered from several serious limitations which should be avoided in planning future research. First, we must know beforehand whether the oil is of high or low toxicity and the extent to which the oil has dispersed or remained in the vicinity of the spill. Secondly, a highly co-ordinated team response is needed to assure that hydrocarbon analyses are made of the bottom sediment and water column at each sampling station. Ideally, each animal selected for pathological examination should be retained for follow-up hydrocarbon analysis. Stations that are selected for intensive study should be sampled at regular intervals to follow progressive change or lack of change in preselected animal species.

The critical need for precise measurements on the effects of oil spills on aquatic resources is as much in evidence today as it was over 50 years ago. Lane and Bauer (1925) wrote: "It would appear, therefore, that oil pollution has considerable effect upon the edible qualities of aquatic animals and may affect the migratory habits of fish; it is detrimental to shellfish by reason of destroying the larval forms and rendering adult molluscs unfit for food. With regard to waterfowl, it appears to be a cause of considerable destruction, rendering the birds helpless through its mechanical action on the feathers. It has been stated that when birds are not actually killed as a result of contact with the oil they are rendered unfit for food due to the oil taint."

Acknowledgments

Histological observations on molluscs were made by Mr. Fred Kern; on fish by Mr. Martin Newman, Dr. Joel Bodammer, and Dr. Robert Murchelano. Crustaceans, sea urchins and starfish were dissected and prepared for histological processing by Ms. Sharon A. MacLean. Mr. John Ziskowski was responsible for the collection, preservation and station data pertaining to all of the animals that were examined by the laboratory staff.

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Histopathological Analyses of Benthic Organisms From the Vicinity of the *Argo Merchant* Wreck

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Abstract

A variety of benthic species were collected on two cruises to the *Argo Merchant* and examined histopathologically.

On the first cruise, two months after the spill, only two crabs were collected. A *Cancer* crab was found dead with a thick deposit of *Argo* oil coating the remnant gut. A hermit crab was found moribund. One *Modiolus* had mantle lesions consisting of round, raised calcified nodules several mm in diameter adjacent to patches of *Argo* oil deposited on the internal shell surface. One starfish of 250 examined had tarballs in the buccal cavity.

In contrast, on the second cruise, seven months following the spill, no oil was seen in eight *Cancer* and ten hermit crabs, 44 starfish and 5 sea cucumbers collected alive. One *Modiolus,* also visibly uncontaminated, had extensive calcium nodule formation on an adductor muscle and surrounding mantle. The findings suggest the effects of the *Argo* oil were, for the most part, within the physiological toleration limits of the macrobenthos, and the overall impact of the oil spill was minor.

Introduction

The wreck of the *Argo Merchant* had all the makings of a major ecological disaster. As the ship broke up on December 21, 1976, approximately 7½ million gallons of oil were released into an area of ocean near Georges Bank, one of the world's most productive fishing grounds. The well known toxic effects of oil on marine organisms, especially when spilled into marine environments from damaged vessels (all references listed), made it imperative to determine the areal extent of oil contamination and its potential effect on the biota near the wreck site.

For these purposes, there were five University of Rhode Island cruises to the area of the *Argo Merchant* wreck; four on the R/V *Endeavor* and one on the F/V *Sideshow.* The authors visited the wrecksite on the last two cruises in February and July, 1977. The purpose of the fourth cruise was to determine, two months after the spill, the areal extent of sediment, phytoplankton, zooplankton and macrobenthos contamination with *Argo Merchant* oil and to deploy bottom drifters. The authors cooperated with Dr. Eva Hoffman and Sheldon Pratt in the collection of sediments and with Renata Polak and Audrey Fillion in the collection of zooplankton. Scott Fortier, USCG, performed the spectrofluorometric analysis of samples of *Argo* oil. The purpose of the July cruise was to determine the extent of persistence of *Argo* oil in the area after seven months. Again, in cooperation with Dr. Eva Hoffman and Sheldon Pratt, most of the February sites were re-sampled.

The purpose of this paper is to present the histopathological findings and conclusions based on these findings on the impact of the *Argo Merchant* oil spill on the macrobenthos dredged from the vicinity of the wreck.

Methods

Benthic organisms were collected by towing a scallop dredge for approximately 10 min. on the bottom. Five dredge samples were collected on February 26, 1977, which was two months after the *Argo Merchant* spill took place. Again on July 24, 1977 four dredge samples were collected from the same vicinity to measure residual effects seven months after the spill. The precise locations and depths of the areas are shown in Table 1. In general, the dredges were made along a southwest to northeast line in the Fishing Rip of the Nantucket Shoals in front of the *Argo Merchant* bow.

All animals were examined grossly for any abnor-

Table 1. Location of the Dredge Samples

Dredge Sample		*Date*	*Time*	*Depth (M)*	*Loran C*	*Latitude/Longitude*
February	1 start	2/23/77	2200	40	37609.9 70091.3	41°03.7′ N 69°23.8′ W
	stop	2/23/77	2238	42	37596.4 70087.2	41°04.9′ N 69°23.0′ W
	2 start	2/24/77	1035	46	37661.8 70104.7	40°59.5′ N 69°27.0′ W
	stop	2/24/77	1103	46	37655.8 70102.4	41°00.2′ N 69°26.8′ W
	3 start	2/24/77	1608	42	37699.3 70095.6	41°00.1′ N 69°32.2′ W
	stop	2/24/77	1630	38	37701.3 70093.5	41°00.5′ N 69°33.0′ W
	4 start	2/26/77	1008	44	37663.3 70105.9	40°59.5′ N 69°26.9′ W
	stop	2/26/77	1034	44	37657.1 70105.0	40°59.6′ N 69°26.4′ W
	5 start	2/26/77	2306	40	37637.1 70094.9	41°02.1′ N 69°26.0′ W
	stop	2/26/77	2330	24	37632.0 70091.5	41°02.9′ N 69°26.0′ W
					Loran A	
July	1	7/24/77	1100	40	3H5-1026 1H3-3695 3H4-6383	41°04.6′ N 69°22.4′ W
	2	7/24/77	1130	38	3H5-1035 1H3-3720 3H4-6370	41°02.2′ N 69°25.2′ W
	3	7/24/77	1200	38	1H3-3730 3H4-6360	41°00.7′ N 60°26.1′ W
	4	7/24/77	1230	40	1H3-3743 3H5-1049 3H4-6347	40°59.0′ N 69°27.8′ W

malities or oil fouling before preservation. Horse mussels were carefully shucked on board and the shell liquor examined for the presence of oil through either a visible sheen or odor. The gonads, colored either red (male) or yellow (female), were examined for extent of development. A bissecting incision was made in each starfish arm to enhance examination and fixation. All macrobenthos were preserved in 10% formalin in seawater. Details of collection and examination of zooplankton samples are presented by the junior author in another paper in this symposium (Polak et al.). Zooplankton samples were divided so that examination of fresh animals could be made on board and preserved specimens could be made in the laboratory. For comparative purposes, zooplankton were preserved in either 10% formalin in seawater alone, 3% glutaraldehyde in seawater alone, 1% osmium tetroxide in 0.1 m collidine buffer alone, or both the formalin and glutaraldehyde treated specimens were post-fixed with the osmium tetroxide solution. In July, macrobenthos were stored in plastic bags on ice on board ship and treated with fixative the following day in the laboratory. Archived samples of all animals were rinsed of the initial fixative and stored in 70% ethanol. For histopathological analysis, tissue samples were rinsed overnight in tapwater, dehydrated in an alcohol-xylene series and embedded in paraffin. Six micron thick sections were prepared, stained with hematoxylin-eosin and observed microscopically for lesions.

Results

There was a diversity of organisms brought up in the dredge on both the February and July cruises, and the predominant macrobenthos in the area were starfish, followed by horse mussels, which were often associated with sponges, tunicates and worms. The fauna are discussed in more detail by Pratt (in these proceedings).

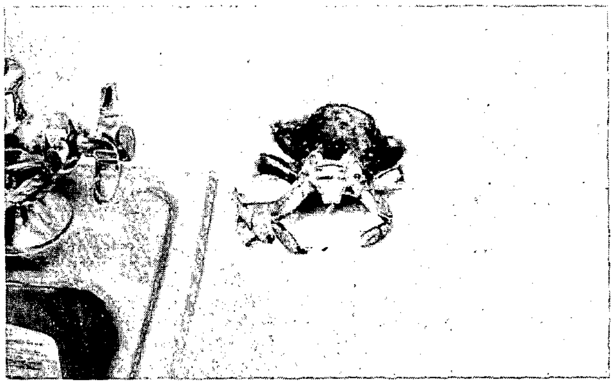

Figure 1. *Cancer crab found dead with stomach remnant coated with Argo oil.*

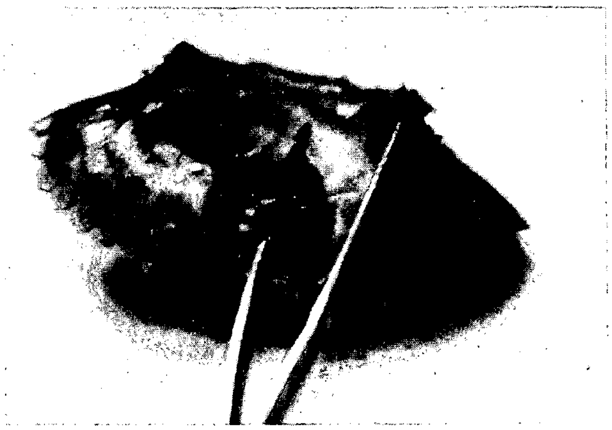

Figure 2. *Forceps placed through Cancer crab mouth parts extended into Argo-oil coated stomach.*

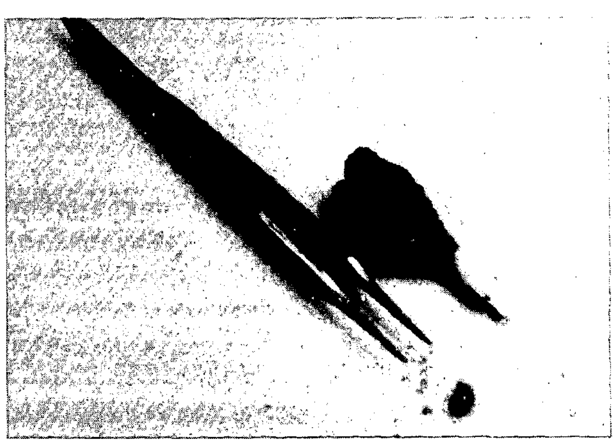

Figure 3. *Cancer crab stomach remnant dissected out to show black tarry appearance.*

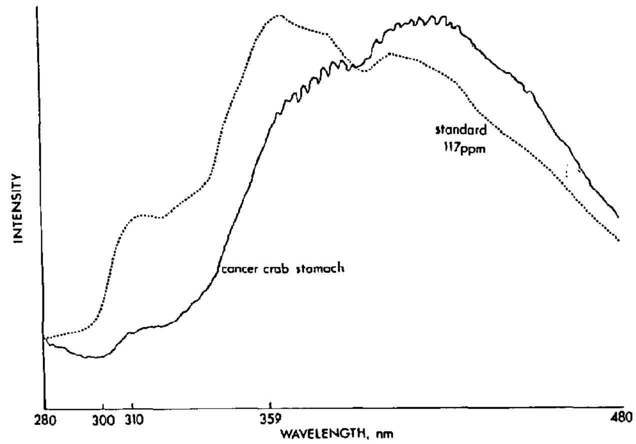

Figure 4. *Comparison of UV spectrofluorometric analyses of Cancer crab stomach and Argo Merchant No. 6 standard oil. The stomach was grossly contaminated with Argo oil in excess of 117 ppm.*

Figure 5. *Appendages of a hermit crab coated with an oil-like substance.*

On the February cruise to the *Argo,* 250 starfish were collected and grossly examined; 33 animals were examined histopathologically. Of these, only one animal showed any evidence of oil contamination, which appeared in the form of several discrete black tarry masses in the buccal cavity. All animals collected were alive and showed no external oil contamination, nor any behavioral indication that they were unhealthy. Only one rock crab, *Cancer borealis,* was collected. This animal was found dead with its carapace only partially attached to its body. No organs were present except a large, approximately 2½ cm wide blackened pouch (Figure 1). Forceps inserted through the mouth entered into this pouch which suggests the black pouch was the remnant of the stomach (Figure 2). When dissected out, the entire stomach remnant was observed to be coated with a blackish-brown tar, the consistency of roof tar (Figure 3). One square millimeter sample was macerated in hexane. The spectrofluorometric analysis of the extract (see technique in Polak et al., these proceedings) indicated that the *Cancer* crab stomach was heavily con-

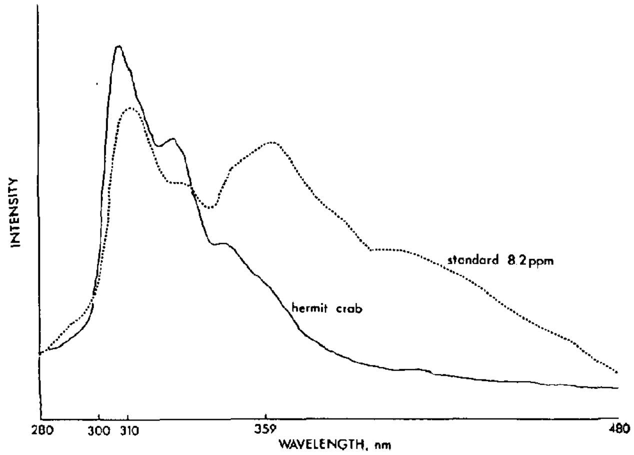

Figure 6. *Comparison of UV spectrofluorometric analyses of hermit crab digestive tract and Argo Merchant No. 6 standard oil. The peaks from the hermit crab roughly match the first two peaks of Argo oil, 8.2 ppm, but the oil constituent of the third peak was absent.*

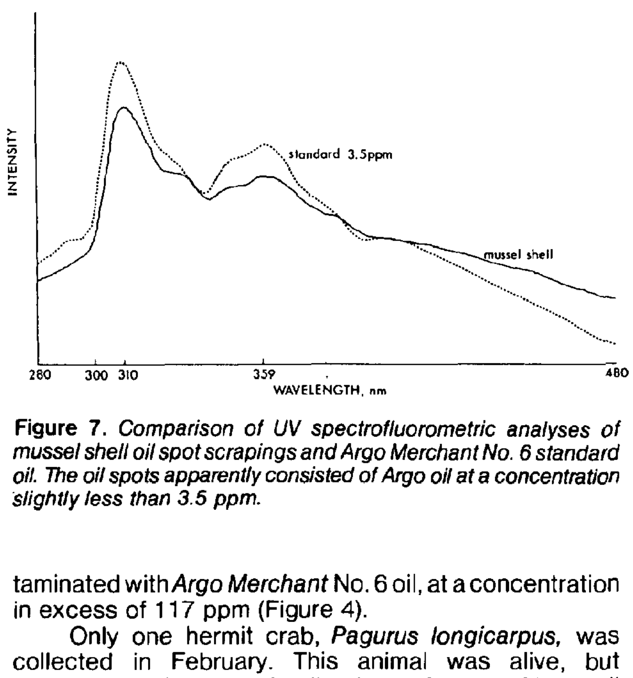

Figure 7. *Comparison of UV spectrofluorometric analyses of mussel shell oil spot scrapings and Argo Merchant No. 6 standard oil. The oil spots apparently consisted of Argo oil at a concentration slightly less than 3.5 ppm.*

taminated with *Argo Merchant* No. 6 oil, at a concentration in excess of 117 ppm (Figure 4).

Only one hermit crab, ***Pagurus longicarpus,*** was collected in February. This animal was alive, but moribund, at the time of collection. It fell out of its shell when picked up from the dredge net. It was incapable of lifting any of its limbs, and only weak movements of its antennae and eye stalks were observed. The appendages of the hermit crab were thinly coated with a black, oil-like material. There were approximately 1 cm wide patches of black material near the mouth parts and on the appendages nearest the mouth parts (Figure 5). Upon dissection, the digestive tract contained a brown fluid which had an oily-waxy feel. Upon spectrofluorometric examination, shown in Figure 6, the first two characteristic peaks of the *Argo* oil standard at 8.2 ppm match the peaks of the hermit crab. However, the third large peak at 360 nm was not present in the hermit crab sample.

Thirty-two horse mussels, *Modiolus modiolus,* were collected on the February cruise and 16 examined histopathologically. Rainbow-like sheens, characteristic of oil contamination, were found on the shell liquor of three mussels. One of these animals had approximately 20 discreet black tarry spots, 1-3 mm in diameter, on the inside of its shell. Some of these spots appeared to be overlayered by a thin, nacre-like material. Several spots were scraped off with a metal spatula, extracted in hexane and examined spectrofluorometrically. As shown in Figure 7, the wavelength "fingerprint" of the scrapings from the shells of the mussel were almost identical to *Argo Merchant* No. 6 standard oil at 3.5 ppm, suggesting these spots were remnants of *Argo Merchant* oil.

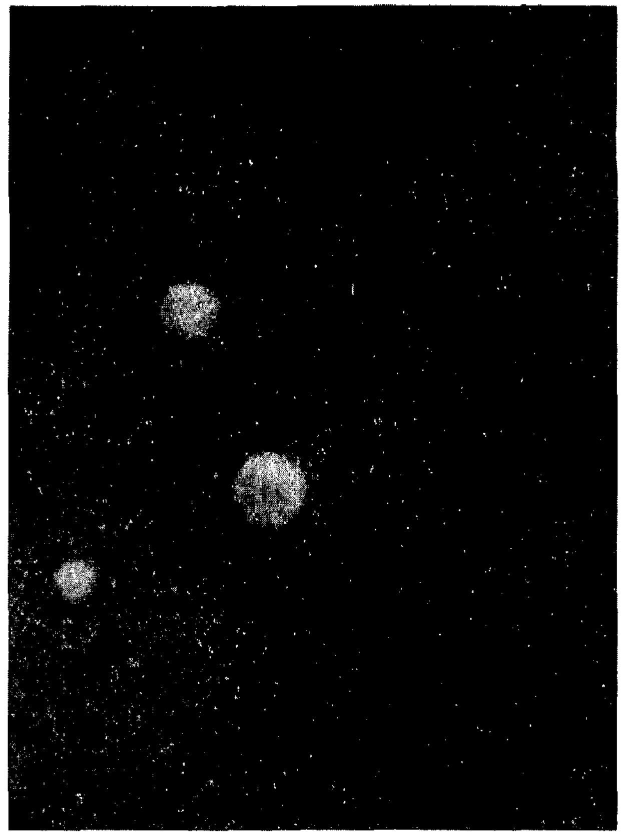

Figure 8. *Round, raised, white, calcified nodules on mantle of horse mussel. Approximately 5X.*

In the places where the overlying mantle of the mussel lay in contact with the spots of oil were found discreet, white, round raised nodules, 1 to several mm in diameter (Figure 8). These were rock-hard to the touch of a metal spatula and required a great deal of pressing force to crush them. Upon gross examination the nodules appeared to be homogeneous and to contain nothing more than a white mineralized material. These were suspected to be calcifications which are part of the nacrezation process that shellfish often produce in response to injury. The nodules dissolved in 40% formic acid, stained blue with hematoxylin and eosin, and appeared to be homogeneous upon histopathologic examination (Figures 9 and 10). There was no evidence that these nodules contained parasites. The nodules were surrounded by an eosinophilic material that, upon examination at 1000X, was

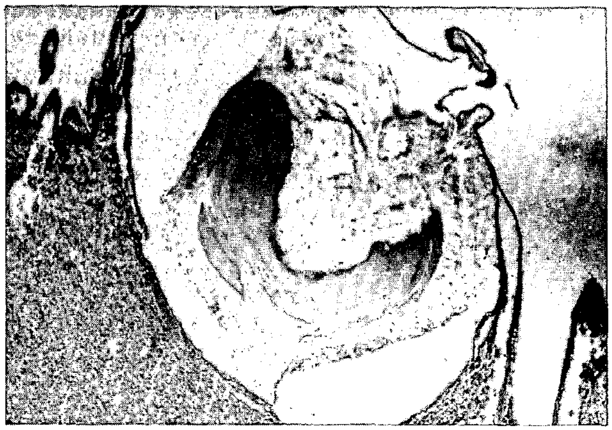

Figure 9. *Cross section of a nodule found on horse mussel mantle, partially decalcified in 40% formic acid. Note absence of parasite and presence of cellular inflammatory response. Approximately 60X, hematoxylin and eosin.*

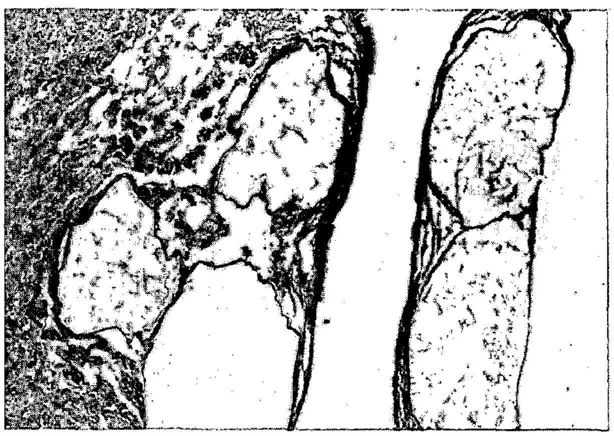

Figure 10. *Completely decalcified horse mussel mantle nodule with associated inflammatory response. Approximately 10X, hematoxylin and eosin.*

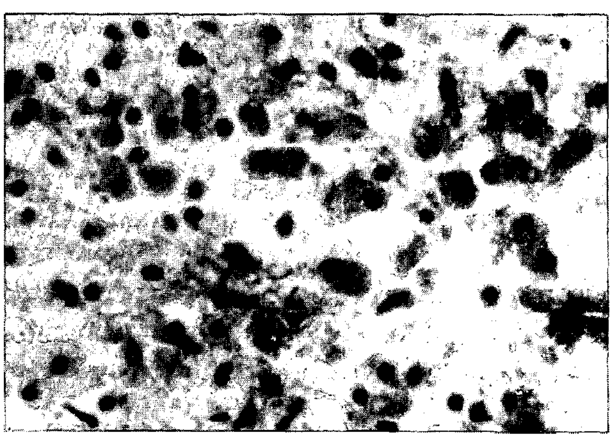

Figure 11. *High power view of inflammatory response showing hemocytes. Approximately 1000X, hematoxylin and eosin.*

Figure 12. *Perivascular inflammation. Approximately 250X, hematoxylin and eosin.*

shown to be accumulations of hemocytes (Figure 11). These accumulations of hemocytes in other mussels and in higher organisms are regarded to be inflammatory reactions, that is, an acute infiltration of hemocytes in response to an injury. Inflammatory reactions were also found in other parts of the body not associated with the oil, especially around blood vessels (Figure 12). Eggs and sperm were present in all mussels and there was no gonadal necrosis found upon microscopic examination (Figure 13). Food was present in the alimentary tract of all horse mussels examined, suggesting no impairment of the feeding mechanism (Figure 13). No histopathological abnormalities were observed in seven sea scallops collected almost due east of the *Argo Merchant* wreck from an area which was not believed to be impacted by the oil spill.

A second trip was made to the area of the *Argo Merchant* oil spill wreck site on July 24, 1977. Again, the purpose of this trip was to collect sediment and benthic organisms for comparison with the February 26 samples. An oil slick of undetermined origin was present in the vicinity of the *Argo* stern, but no oil was found in sediments (Hoffman and Quinn, these proceedings) or on zooplankton (Polak et al., these proceedings).

Over 400 starfish were collected alive and apparently in good physical condition. No gross or microscopic

Figure 13. *Horse mussel gonad is replete with eggs and intestine contains food. Approximately 160X, hematoxylin and eosin.*

lesions were discovered upon histopathological examination of 44 starfish.

Of the 24 horse mussels collected, 12 were examined histopathologically. Approximately 60% of the adductor muscle of one horse mussel was covered with the same type of round, raised, white, apparently calcified nodules as described above. However, the organism's shell was intact and closed upon collection, suggesting the lesion did not severely affect the function of the adductor muscle. Also, upon histopathologic examination, these calcified nodules were not accompanied by any inflammatory response, suggesting that this lesion was a response to an injury that had occurred earlier in the life of the animal and that had since healed. It is not known whether this lesion was formed in response to exposure to *Argo Merchant* oil, although it is certainly possible, as it was similar to the one lesion found in February that was apparently the result of the *Argo Merchant* oil. Again, as in February, there were no abnormalities found in the reproductive organs of the horse mussels collected in July.

In contrast to the February samples, the July samples contained a greater number of crustaceans. Eight rock crabs and 10 hermit crabs were collected in July as compared to only one of each in February. These organisms were collected alive and appeared to be in good physiological condition, which contrasted to the organisms found in February that were dead or moribund. Also in July there were 5 sea cucumbers collected where there were none collected in February. The area where the scallops were collected in February was not visited in July.

Discussion

Argo oil was found to be persistent in the environment of the *Argo* wreck for at least two months after the spill. The oil had an impact on the macrobenthos, but less so in July than in February. Although the effects will never be entirely known, and although there may possibly develop chronic, long term effects, there is reason to believe the effects of the *Argo* on the macrobenthos were minor.

Even though collections were made more than two months after the wreck itself, there was still evidence of *Argo Merchant* oil contamination in the immediate area of the wreck in both sediment and zooplankton as determined by spectrofluorometric analyses of fresh specimens on board. In February, 1977, sediment from 30 sites were taken and 26% contained *Argo* oil (Hoffman and Quinn, these proceedings). Of 22 zooplankton sampling sites, 32% had a trace amount of *Argo* oil and 64% were heavily contaminated (Polak et al., these proceedings). Our findings of oil contamination in two crabs and several mussels also indicated *Argo* oil reached the bottom and persisted in the area of the wreck.

It is interesting to note that the hermit crab found in February, although contaminated with an oil, did not have the characteristic *Argo Merchant* No. 6 UV absorption spectrum. The characteristic third peak of *Argo* oil was not present in the hermit crab. This suggests that the hermit crab may have been exposed to either the *Argo* cutter stock, which was the lighter oil used to dilute the No. 6, or it may mean that the hermit crab was able to partially metabolize some of the *Argo* No. 6 oil, or the hermit crab may have been contaminated by some other oil of unknown origin present in the area.

There were marked differences in our findings in February and July. In February, there was visible oil contamination of zooplankton, two crabs, and several mussels, while there was no visible oil contamination of those species collected in July. In February, one mussel was found with discreet calcified, inflamed lesions. In July, one mussel was found with calcification, but not inflammation. In February, there was evidence of oil impact on the crab population. One crab was found dead and one crab was moribund and both were contaminated with oil. In July, the findings did not indicate any crab mortality in the area. The eighteen crabs collected were clean and apparently healthy, as compared to finding only two crabs which were severely affected in February. It is not known whether the increased number of crustaceans found in July reflect sampling variability, seasonal changes in the populations, or whether they reflect a return of these organisms which might have fled in response to the *Argo Merchant* oil spill.

In both February and July there was no microscopic evidence of impairment of gonadal development. This does not rule out the possibility of mutagenic or teratogenic effects, which apparently could have occurred to fish eggs exposed to *Argo* oil (Longwell, these proceedings).

Based on our observations and investigations on two visits to the *Argo* wrecksite, the authors are led to believe the level of oil toxicants that reached the bottom were, for the most part, within the physiological toleration limits of the macrobenthos.

The apparent minor effects of the *Argo* oil spill can be explained in terms of established toxiocological principles. That is, the toxicity of a particular substance to an organism is dependent upon the amount and duration of exposure.

The immense volume of ocean can be considered to have acted as an extremely large diluent of the potentially toxic oil, thus reducing the amount of oil that reached the macrobenthos. Also, the ocean currents are in a constant state of flux in the shoal area. The tidal flow rates through the Nantucket Shoals are great (Pratt, these proceedings), and there were storms with high seas following the spill that further acted to disperse the oil, and reduce the time of exposure to it. Therefore, it is likely that only a small portion of the *Argo* oil ever reached the bottom, of which a smaller portion still would have impacted the macrobenthos. The results obtained by Hoffman and Quinn (these proceedings) indicated that little oil actually was found in the bottom sediments supporting macrobenthos. Our own results indicated that oil reached the bottom, but affected only six animals of hundreds collected. It can also be speculated that the effects were minor because the majority of animals were able to escape exposure to what oil did reach the bottom. The crustaceans could have moved out of the spill area and the mussels could have remained closed until the oil was removed by tidal action. This could explain why so few affected animals were found and why there were many more crustaceans present in July. In the final analysis, it is impossible to reach a conclusion as to the magnitude of the effect of the *Argo Merchant* oil spill. Only a very small portion of a very large area that was impacted was sampled, and our samplings did not begin until two months after the spill. This, of course, was due to the large number of scientists and observers interested in studying the spill and the limited number of research vessels and available space on them to accommodate everybody. When interpreting our results, keep in mind that there is no information on the status of the benthos at the time of the spill or immediately after, when acute toxic effects would have most likely occurred. In the case of future oil spills, it is recommended that there be sufficient contingency planning to get as many investigators to the scene as quickly as possible so that the degree of effect can be precisely determined.

Acknowledgments

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Some Physiological Effects of the *Argo Merchant* Oil Spill on Several Marine Teleosts and Bivalve Molluscs

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Abstract

Subsequent to the oil spill from the tanker *Argo Merchant*, two cruises provided animals for physiological and biochemical testing. Blood samples were taken from a variety of teleost species, and although the sample number for most species was too small for valid statistical analysis, there did appear to be a disruption of serum ions in winter flounder, *Pseudopleuronectes americanus*, yellowtail flounder, *Limanda ferruginea*, and haddock, *Melanogrammus aeglefinus*. Serum osmolality, sodium, and potassium values were variously depressed in fish collected from oil-impacted areas, as compared to fish from clean or unimpacted areas.

Ocean scallops, *Placopecten magellanicus*, and horse mussels, *Modiolus modiolus*, collected during the first cruise from oil-impacted areas had depressed gill-tissue oxygen consumption, but normal values were recorded from scallops collected during a second cruise six weeks later. Serum sodium and calcium levels of scallops collected from oil-impacted areas during the second cruise were elevated, as compared to scallops collected from clean areas.

Malic dehydrogenase activity of scallop muscle was significantly decreased in scallops from oil-impacted areas. Lactate oxidation was also significantly lower in these animals, although pyruvate reduction, catalyzed by the same enzyme, remained the same. Both observations suggest a possible weakening of the ability to shift to anaerobiosis.

Introduction

The effects of petroleum hydrocarbons on a variety of marine animals have been studied extensively by means of controlled laboratory exposures. Several recent publications provide extensive reviews on these studies (Emery, 1972; Moore and Dwyer, 1974; Anderson, 1977). By contrast, measurements performed on animals taken from their natural habitat following an oil spill are rare, and grounding of the tanker *Argo Merchant* with its subsequent release of 7.7 million gallons of No. 6 fuel oil into the surrounding waters provided an unusual opportunity for a series of such measurements.

This report, therefore, attempts to compare some aspects of the physiology and biochemistry of several bivalve mollusc and finfish species taken from oil-impacted areas to those of animals taken from adjacent areas untouched by the oil spill. We were able to collect only limited numbers of any one species, however, and we present our data here with correspondingly limited statistical confidence. Nevertheless, because post oil-spill physiological data, however incomplete, are rare, and because the data presented here do suggest some possibly valuable indicators of metabolic stress, we feel that the information will be a useful supplement to the existing oil-exposure literature and may form a base for future studies of a similar nature.

A number of physiological processes have been measured in recent years as indicators of sublethal stress. Among these, the parameter that has received the greatest attention in the literature is the rate of oxygen consumption. A review by Anderson (1977) recently emphasized the usefulness of respiratory measurements in oil pollution studies. Measurements of respiration have also been recommended by researchers of the NSF-IDOE Biological Effects Program as a valuable indicator of pollutant stress (Giam, 1977). Hematological effects of pollutants have received less emphasis; however, several recent publications have demonstrated the usefulness of this type of measurement in physiological studies related to environmental pollution (Calabrese et al., 1975; Dawson, in press).

Enzymes involved in carbohydrate metabolism are said to constitute the largest fraction of enzymes affected by acute oil exposure (Heitz et al., 1974). The posterior adductor muscle of the blue mussel, *Mytilus edulis*, for example, was depleted of glycogen stores after the animal's experimental exposure to oil, a loss of energy that is normally held for use in gametogenesis, and that is untapped even during prolonged starvation (Dunning and Major, 1974). The object of our biochemical testing in this study, therefore, was to measure the relative activities of regulatory glycolytic enzymes, as well as representative enzymes of the tricarboxylic acid cycle, the pentose shunt, and nitrogen metabolism. Most closely examined in bivalve adductor muscle were both forward and reverse reactions of malate dehydrogenase (E.C. 1.1.1.37; MDH) and D-lactate dehydrogenase (E.C. 1.1.1.28; LDH). Induction of glycolytic enzymes generally reflects a mobilization of energy reserves, and induction of pentose shunt enzymes reflects increased biosynthetic rates, both of which might reasonably be expected, at least initially, in sublethally stressed animals. During anaerobiosis in invertebrates, MDH and LDH activities are respectively induced and repressed (Hochachka and Somero, 1973), a pattern that has also been observed in the tissues of lobsters, *Homarus americanus*, stressed by low salinity (Gould, unpub.)

Methods

Teleost and molluscan samples for this study were collected during the 4-10 January 1977 cruise of the NOAA R/V *Delaware II* and the 18-26 February 1977 Polish R/V *Wieczno* cruise. Samples were taken from both oil-impacted and adjacent clean areas. Ocean scallops *(Placopecten magellanicus)* and horse mussels *(Modiolus modiolus)* were collected with a Digby dredge and maintained alive on the ship in running seawater. They were transported to the Milford Laboratory on ice and then transferred to running ambient seawater (about 26-28 ppt salinity, 2-5°C) for up to one week prior to testing.

For oxygen-consumption studies, a single gill was dissected from each bivalve and placed in a 15-ml Warburg-type flask. Each flask contained 5 ml of seawater at a salinity of 27 ppt. Oxygen consumption of each gill was monitored over a 4-hr period in a Gilson differential respirometer at 10°C. Oxygen consumption rates were calculated as microliters of oxygen consumed per hour per gram, dry weight, of gill tissue ($\mu\ell$ O_2/hr/g), corrected to microliters of dry gas at standard temperature and pressure.

For hematological measurements, blood was collected from scallop adductor muscles using a 3-ml syringe and a 20-gauge needle. Each blood sample was centrifuged for 5 min at 12,000 x g and the serum removed for measurements of sodium, potassium, calcium, and osmolality. Sodium, potassium, and calcium were analyzed with a Coleman Model 51 flame photometer. Serum osmolality was measured on an Advanced Model 3L osmometer using 0.2-ml samples. Teleost blood samples were taken by cardiac puncture from live fish immediately after trawl capture. Again, a 3-ml syringe with a 20-gauge needle was used and the sample centrifuged at 12,000 x g. The samples were then frozen for later analysis at the Milford Laboratory. Serum sodium, potassium, calcium, and osmolality were measured using the same instrumentation as for the scallop serum.

For biochemical testing, the adductor muscles were excised from the scallops that were transported live to the laboratory, then kept frozen (-29°C) until analysis. Other scallops were frozen whole at sea just after collection and transferred frozen to the laboratory. They were thawed just enough to enable excision of the adductor muscles, which were then packaged and kept frozen under the same conditions. For enzyme measurements, the muscle samples were made 1:1, w/v, with an iced 0.88 M sucrose solution containing dithiothreitol (1 mM). The preparations were vigorously ground in a glass homogenizer with 20-30 mg of 25-μm glass powder, and the resulting paste centrifuged for 1 hr at 4°C and 17,000 x g. After centrifugation, the clear supernates (2X prep) were transferred with Pasteur pipettes to cold test tubes and kept on ice throughout the analysis. For the malate oxidation (MDH) and both LDH reactions, the preparations were diluted 1:4 for a final 10-fold dilution (10X prep), and for oxaloacetate reduction (MDH), the tissue preparations were diluted 1:49 for a final 100-fold dilution (100X prep). Preparations of teleost tissues were: pooled brain samples, 1:9 in H_2O, w/v; pooled kidney samples, 1:9 in H_2O, w/v; and gonad samples, 1:4 in 0.88 M sucrose - 1 mM DTT*, w/v. Centrifugation was at 4°C and 28,000 x g for 60 min for kidney and brain preparations, and at 40,000 x g for 45 min for gonad preparations. Tissue pools were from 2 animals each.

All solutions were made with doubly glass-distilled water, and all reaction rates were read at 340 nm with a double-beam ratio-recording spectrophotometer, chamber temperature 25°C, in cuvettes having a 10-mm pathlength. Reaction volume was 3.00 ml. Reaction rates were followed on a linear-log potentiometer recorder and calculated from the fastest portion of the curve.

For the assays, reactant concentrations (mM) were:

(1) oxaloacetate reduction (MDH): buffer, pH 9.0, 90 glycine and 0.9 disodium EDTA* dihydrate; 0.15 reduced NAD*; 1.0 oxaloacetic acid, cis-enol form; and 0.10 ml 100X enzyme prep to start;

(2) malate oxidation (MDH): same buffer as for (1); 0.30 NAD; 6.7 L-malic acid, neutralized with KOH; and 0.10 ml 10X enzyme prep to start;

(3) pyruvate reduction (LDH): 90 phosphate buffer, pH 7.5; 0.10 reduced NAD; 10 sodium pyruvate; and 0.10 ml 10X enzyme prep to start;

(4) lactate oxidation (LDH): 90 Tris* buffer, pH 8.0; 0.30 NAD; 133.3 DL-lactic acid, lithium salt; and 0.10 ml 10X enzyme prep to start;

(5) malic enzyme (ME) (E.C. 1.1.1.40): 81.3 HEPES* buffer, pH 8.0; 1.0 $MnCl_2$; 0.4 NADP*; 0.20 ml 2X enzyme prep; and 6.7 L-malic acid, neutralized with KOH, to start ME reaction. ME activity was corrected for endogenous NADP reduction by subtracting the reaction rate measured before addition of the malate substrate.

All data were analyzed statistically by using the Student's "t" test.

Results

The mean gill-tissue oxygen consumption rate of scallops collected from sites within the spill area during the January cruise was 594 $\mu\ell$ O_2/hr/g (n = 7) (Figure 1). This value is considerably lower than the 675 $\mu\ell$ O_2/hr/g (n = 5) rate found in scallops from adjacent unimpacted areas. The respiratory rates of scallops collected from oil-contaminated areas in February had a mean value of

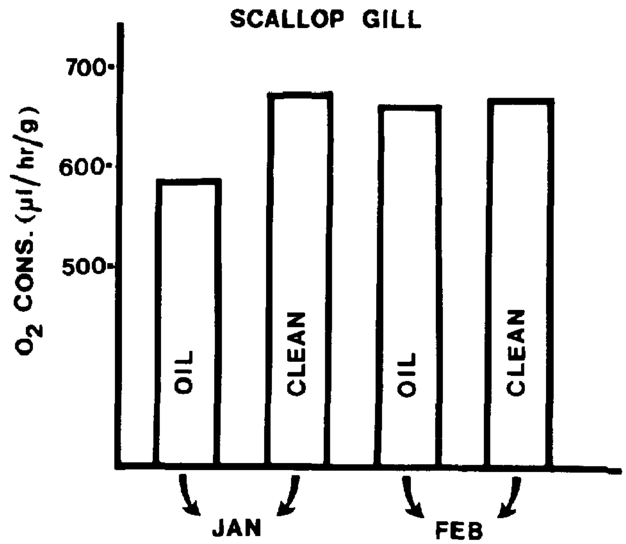

Figure 1. *Gill-tissue oxygen consumption values of sea scallops, Placopecten magellanicus, taken from oil-impacted areas (n = 7 and 9) and adjacent clean areas (n = 5 and 9) in January and February, 1977.*

651 μl O_2/hr/g (n = 9) and were similar to the January control values from unimpacted areas. The February control site animals had a mean rate of 654 μl O_2/hr/g (n = 9). The standard errors for those four groups were similar, ranging from 28-34. Only 2 mussels were collected from an oil-contaminated area during the January cruise. The mean oxygen-consumption rate of gills from these bivalves was 451, a value lower than the mean value of 596 μl O_2/hr/g of 6 mussels collected from an adjacent clean area. No mussels were collected during the February cruise.

Table 1. Serum measurements made on ocean scallops, *Placopecten magellanicus,* from oil-impacted areas and adjacent clean areas. Osmolality values are in mOsm/kg; others are in meq/1.

Test	*Clean*	*N:18*	*Oil*	*N:26*	*P*
Osmolality	819	SE 2	818	SE 2	NS
Sodium	365	2	380	2	P<.001
Potassium	12.5	0.3	12.5	0.3	NS
Calcium	16.5	0.2	17.5	0.2	P<.05

Serum samples taken from scallops from oil-impacted areas during the February cruise showed some serum ion disruption. Both serum sodium and calcium levels were significantly elevated, whereas osmolality and potassium were unaffected (Table 1).

MDH activity was significantly depressed in the adductor muscle of scallops frozen whole at sea after being taken from oil-impacted areas, in comparison to the scallops from clean areas (Table 2). Lactate oxidation was also lower, but pyruvate reduction, catalyzed by the same enzyme (LDH), remained unchanged. Malic enzyme activity was also significantly depressed. For scallops brought back live to the laboratory and dissected there for analysis, however, there were no significant differences between animals from oil-impacted areas and those from clean areas, when the same activities in the same tissue were compared (Table 3). The only observation of statistical significance in these animals was that lactate oxidation increased 20- to 30-fold over animals frozen whole at sea (627 and 469, as compared with 36 and 14 in Table 2), while pyruvate reduction decreased by almost half (83, as compared with 141 and 159). As a result, the PR/LO values averaged 0.2, in contrast to 3.9 and 14.3 for animals frozen immediately at sea after being taken from clean or from oil-impacted areas, respectively.

Of the teleost species tested biochemically, most belonged to one of three families: the pleuronectids, the clupeids, and the gadoids. The first group was represented by yellowtail flounder *(Limanda ferruginea)* and winter flounder *(Pseudopleuronectes americanus);* 6 animals each were taken from clean areas and 6 each from oil-impacted areas. Pools were from 2 animals each for kidney and for brain. Gonads were prepared individually, because of the variables of sex and degree of gonad maturation. The clupeids were represented by the alewife *(Pomolobus pseudoharengus),* 3 fish from clean and 6 fish from oil-impacted areas, and the blueback *(Pomolobus aestivalis),* 1 specimen only, from a clean area. The third group was represented by cod *(Gadus morhua),* 4 fish from clean areas and 1 from an impacted area, and haddock *(Melanogrammus aeglefinus),* 1 from a clean and 2 from an impacted area. Single specimens were also taken of other species representing other families. The brain, kidney, and gonad preparations were

Table 2. Sea scallops, *Placopecten magellanicus,* collected from clean and from oil-impacted areas during first cruise of *Delaware II* in January, 1977, frozen whole at sea, and thawed for dissection and analysis in April, 1977. Units of enzyme activity: reduction, µmoles NADH oxidized/min/mg protein; oxidation, µmoles NAD reduced/min/mg protein; malic enzyme, µmoles NADP reduced/min/mg protein.

	Clean (N:6)			*Oil-impacted (N:10)*			
Enzyme	$\bar{x}$	*SE*	*(range)*	$\bar{x}$	*SE*	*(range)*	*P*
MDH: oxaloacetate reduction	3128	423	(2062-5014)	1118	92	(825-1651)	<0.001
MDH: malate oxidation	59	15	(34-131)	18	2	(10-29)	<0.05
OAR/MO	58.5	5	(38.3-70.3)	69.2	8.8	(32.8-127.0)	
LDH: pyruvate reduction	141	24	(67-233)	159	11	(119-237)	
LDH: lactate oxidation	36	9	(24-71)	14	2	(5-24)	<0.01
PR/LO	3.9	0.9	(1.5-6.4)	14.3	2.1	(5.7-23.8)	<0.01
MDH (OAR)/LDH (PR)	26.1	5.7	(11.2-46.4)	7.3	0.7	(4-11)	<0.001
Malic enzyme	23	4.3	(10.6-38.5)	11.7	1.1	(5.5-17.8)	<0.01

Table 3. Scallops, *Placopecten magellanicus,* collected from clean and from oil-impacted areas during first cruise of *Delaware II* in January, 1977. They were maintained alive on the ship in running seawater (3-4 days), returned to the laboratory on ice (5 hr), and transferred to running ambient seawater for up to 1 wk before dissection and analysis. Units of activity are as in Table 1.

	Clean				Oil-impacted			
Enzyme activity	*(N)*	*x*	*SE*	*(range)*	*(N)*	*x*	*SE*	*(range)*
LDH: pyruvate reduction	(13)	83	24	(15-271)	(6)	83	12	(43-131)
LDH: lactate oxidation	(7)	627	63	(414-913)	(5)	469	31	(416-582)

Table 4. Serum measurements made on yellowtail flounder, *Limanda ferruginea,* and winter flounder, *Pseudopleuronectes americanus,* from oil-impacted areas and adjacent clean areas. Osmolality values are in mOsm/kg; others are in meq/1.

	Yellowtail flounder serum				
Test	*Clean*	*N:7*	*Oil*	*N:17*	*P*
Osmolality	473	SE 34	425	SE 11	P<.05
Sodium	208	12	193	4	P<.05
Potassium	7.26	1.10	7.07	0.73	NS
Calcium	6.30	0.38	5.97	0.30	NS
	Winter flounder serum				
	Clean	*N:5*	*Oil*	*N:5*	*P*
Sodium	193	SE 7	205	SE 2	NS
Potassium	7.08	0.41	3.97	0.13	P<.001
Calcium	5.74	0.40	5	0.38	NS

Table 5. Serum measurements made on herring, *Clupea harengus,* and alewife, *Pomolobus pseudoharengus,* from oil-impacted areas and adjacent clean areas. Osmolality values are in mOsm/kg; others are in meq/1.

	Herring serum				
Test	*Clean*	*N:9*	*Oil*	*N:7*	*P*
Osmolality	530		555		NS
Sodium	245		241		NS
Potassium	7.44		9.45		NS
Calcium	6.51		6.66		NS
	Alewife serum				
	Clean	*N:6*	*Oil*	*N:9*	*P*
Osmolality	527		497		NS
Sodium	230		228		NS
Potassium	9.24		7.97		NS

Table 6. Serum measurements made on haddock, *Melanogrammus aeglefinus,* from oil-impacted areas and adjacent clean areas. Osmolality values are in mOms/kg; others are in meq/1.

Test	*Clean*	*N:6*	*Oil*	*N:14*	*P*
Osmolality	453	SE 31	385	SE 5	P<.05
Sodium	200	15	179	3	P<.05
Potassium	8.31	1.20	7.36	0.38	P<.05
Calcium	3.92	0.92	3.83	0.50	NS

variously examined for glucose phosphate isomerase (E.C.5.3.1.9), pyruvate kinase (E.C.2.7.1.40), glucose-6-phosphate dehydrogenase (E.C.1.1.1.49), isocitrate dehydrogenase (E.C.1.1.1.42), and aspartate aminotransferase (E.C. 2.6.1.1), as well as for MDH and LDH. Although there were insufficient data for each species for statistical comparison of clean and oil-impacted areas, each tissue-specific enzyme seemed to fall within the same range for each teleost family (gadoids, clupeids, pleuronectids) over all collection sites.

Results of the teleost serum studies are presented in Tables 4, 5, and 6. Sodium was depressed in yellowtail flounder from oil-impacted areas, as was osmolality; winter flounder sodium was elevated, but osmolality was not measured (Table 4). No differences in osmolality, sodium, or potassium were detected in either alewives or herring when fish from oil-impacted and clean areas were compared (Table 5). The limited number of haddock tested showed depressed serum osmolality, sodium, and potassium levels in fish collected from oil-impacted areas, as compared to fish from an adjacent unimpacted area (Table 6).

Discussion

The respiratory results of this study give some indication of stress due to oil exposure. The seven scallops from oil-impacted areas showed considerable depression of gill-tissue oxygen consumption when compared to scallops from adjacent clean areas. The small number of bivalves sampled precluded meaningful statistical analysis, but does give an indication of oil-related respiratory stress. Other investigations have reported respiratory alterations in various marine animals, including bivalve molluscs, after exposure to oil or oil fractions (Brocksen and Bailey, 1973; Avolizi and Nuwayhid, 1974; Gilfillan, 1975; Percy, 1977). Scallops collected one month later showed no signs of respiratory stress. They may have recovered from oil exposure or may never have been exposed even though they were collected from areas where an oil slick had been reported. A recovery seems more probable; other investigators have reported respiratory recovery in marine animals following their return to clean water after oil exposure (Brocksen and Bailey, 1973; Anderson et al., 1974). These scallops had elevated plasma sodium and calcium levels, an observation suggesting that they had indeed been exposed to the oil.

Because bivalves in general are osmoconformers, it is not surprising that oil exposure did not affect serum osmolality in scallops. Anderson and Anderson (1975) reported similar results for the American oyster using a short-term laboratory exposure to oil. Although total osmolality did not change in our oil-impacted animals, there were changes in some of the components. Serum sodium rose from 365 meq/1 to 380 meq/1 in animals from the oil-impacted area. Calcium also increased in oil-impacted animals to 17.6 meq/1, compared to 16.9 meq/1 in controls.

In view of the suggestion by Sabo and Stegeman (1977) that oil may alter membrane structure, teleost osmo- and ion-regulation would appear to be among the more reasonable areas of study for future oil-spill research. However, information on how oil exposure affects these processes in any animal is extremely limited. The fish studied exhibited a species-variable response to oil exposure. Two of them, the herring and the alewife, had no significant oil-induced changes in any of the variables tested. In the species that showed a change, serum osmolality, sodium, or potassium went from a point below that of the surrounding seawater to an even lower point. In fishes tested for serum calcium, there was no change. The possibility of utilizing calcium stored in bone and other tissues may make calcium regulation in fish less susceptible to disruption by oil exposure than sodium and potassium regulation (Fleming, 1967; Fleming, Brehe, and Hanson, 1973).

The bivalve adductor muscle is a sensitive indicator of anaerobiosis - more so than mantle tissue (Livingstone, 1976) - and lends itself especially well to biochemical examination. Of the bivalves collected, only the scallop was taken in sufficient numbers for statistical analysis. Some were frozen whole at sea immediately after collection, and others were brought back to the laboratory for analysis, a circumstance that allowed a practical comparison of methods.

The lowered activities of MDH and ME observed in the adductor muscle of sea-frozen scallops taken from oil-impacted areas, as compared with those taken from "clean" areas (Table 3), could be attributed to any of several possible factors: 1) inhibition of the animal's capacity to maintain a normal metabolism (MDH repression); 2) a slowed feeding rate (low ME), either in concert with or as a consequence of a lowered metabolic rate, another sign of which was the depressed rate of gill-tissue oxygen consumption; or even 3) a weakening of the ability to shift to anaerobiosis (MDH and lactate oxidation down, but pyruvate reduction unchanged), in defense against ingestion of toxicants. Hammen (1969) has pointed out that the PR/LO ratio indicates the probability of lactic acid production, which must be shut down during anaerobiosis. We hesitate, however, to draw any firm conclusions. Although the data are statistically valid, the sample number is small, and until these observations can be confirmed by future measurements under similar circumstances, no great significance should be attached to them.

More useful at this point, perhaps, is the comparison of the data obtained from animals frozen whole at sea after capture (Table 2) with the data obtained from scallops returned live to the laboratory for dissection and analysis (Table 3). The latter group of scallops was held in clean seawater aboard ship until brought to shore (2-3 days), then transported on ice to the Milford Laboratory (5 hrs), where the animals were placed in flowing seawater for up to one week before dissection. It is a plausible assumption that the animals at least partially cleared themselves during the shipboard holding period, and that they shifted toward anaerobiosis during their transport to the laboratory. There was a greater than 20-fold increase in lactate oxidation in these animals, as compared with the animals frozen at sea, and a drop in pyruvate reduction, both mechanisms preventing the dead-end accumulation of lactic acid during anoxic glycolysis. It is our belief that data from animals frozen at sea more accurately represent the biochemical state of these animals in their native habitat, and our future sampling procedures will be based on this observation.

No differences could be detected in enzyme activities of kidney, brain, or gonad taken from fish collected from clean areas, as compared with those of fish taken from oil-impacted areas. Each tissue-specific enzyme fell within the same range for each teleost family (gadoids, clupeids, pleuronectids) over all collection sites, however, and the information will be used to form the nucleus of a baseline data bank. In this respect, it will be important to have consistent sampling of a selected number of representative species at different seasons of the year, together with information on water temperature, salinity, and depth of catch.

The foregoing results indicate that bivalves and teleosts from an area perturbed by an oil spill experience a variety of physiological alterations. Although it would be scientifically unsound to draw any definite conclusion or to make any general statements or assumptions from such limited data, it would be equally unwise to ignore the indications of stress that show in these data. Similar testing must be conducted after future oil spills before definitive conclusions can be made. The Northeast Fisheries Center of the NMFS is initiating a program of physiological monitoring to coordinate and carry out such studies. This program, called Ocean Pulse, is designed to monitor and assess the health of the ocean's living resources on the continental shelf of the northeast Atlantic (Pearce, 1977; Sherman, 1977). Such an effort will coordinate short-term assessment studies in response to a pollution event such as the *Argo Merchant* oil spill, and provide for long-term physiological monitoring of a variety of representative marine species. The results obtained in this study are valuable as "test phase" data and will be used as such in the Ocean Pulse program planning and execution.

Note: Use of trade names is to facilitate description and does not imply endorsement by the National Marine Fisheries Service, NOAA.

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*Abbreviations used are: EDTA, ethylenediamine tetraacetic acid; NAD, nicotinamide adenine dinucleotide; NADP, nicotinamide adenine dinucleotide phosphate; Tris, tris (hydroxymethyl) aminomethane; DTT, dithiothreitol; HEPES, (*n*-2 hydroxyethyl)-piperazine (*n*′-2-ethane) sulfonic acid.

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Observations on *Argo Merchant* Oil in Zooplankton of Nantucket Shoals

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Abstract

Zooplankton samples were taken in February, July and December 1977, on Nantucket Shoals, following the *Argo Merchant* spill.

Visual observations of apparent oil in zooplankton were followed by Ultra Violet Spectrofluorometric analysis to establish relative levels of contamination. Of 22 sites sampled in February, zooplankton samples from 14 showed significant concentrations of oil. Frozen samples collected in February, July and December 1977 were also analyzed using the spectrofluorometric method. Samples taken in February, and preserved in formalin, were also examined for comparison with the frozen samples.

Histopathological examinations of hematoxylin and eosin stained organisms from February samples indicated an oil-like material present in the area of the gut of some crustacean zooplankton. Fluorescence microscopy was used in an attempt to identify the oil-like globules.

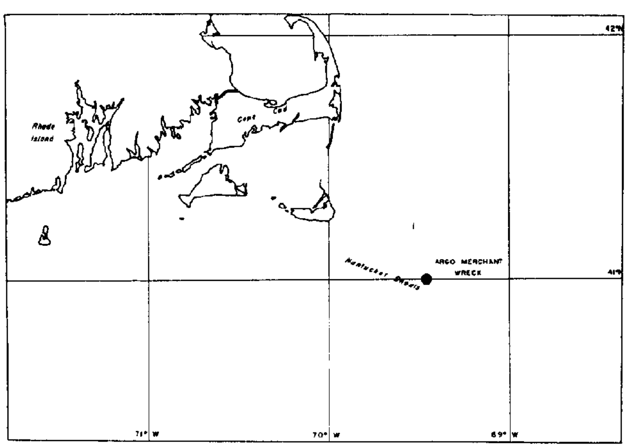

Figure 1. *Nantucket Shoals, site of the wreck.*

Introduction

Following the wreck of the *Argo Merchant* tanker on Nantucket Shoals (Figure 1), on December 15, 1976, and the subsequent release of approximately 7.7 million gallons of No. 6 fuel oil, a survey was carried out, February 21 to 25, 1977, to investigate the possibility of persistent contamination of zooplankton in the area of the spill.

Observations on the marine communities immediately after the spill (Dec. 22-24) were conducted by the personnel of the Northeast Fisheries Center of the National Marine Fisheries Service. At that time, the oil slick was still in the area of the wreck, and at 6 of the 11 stations sampled, copepods fouled by an oil-like material were observed. The contamination was classified by NMFS as:

a) external; smudges on the exoskeleton.

b) mandibular; particles adhering to feeding appendages or tar stains on mandibles.

c) apparent oil particles which had been ingested and were present in the gut.

During the *Endeavor* 005 cruise, February 21-25, 1977, we sampled the zooplankton at 22 stations around the wreck. On July 22, 1977, 6 of the February stations were repeated and a new station was added. On December 15, 1977, another 4 of the February stations were sampled by NMFS at our request.

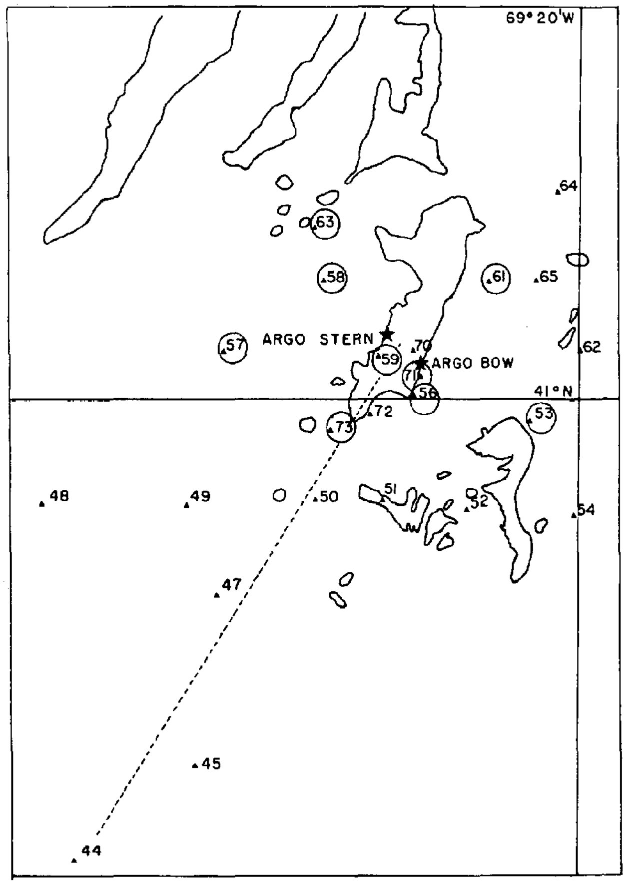

Figure 2. *Chart of sites sampled.*

Methods

During 21-25 February, oblique tows were taken first with 0.5 meter nets of 0 and 6 mesh size, and later in the cruise with large 61 cm bongos of corresponding mesh size. In July and December, double oblique tows were made with paired 61 cm bongos and the same mesh sizes. The zooplankton collected was examined superficially under a dissecting microscope. A number (~5-15 of organisms were removed for subsequent histological examination. From the remainder of the net contents, samples of approximately 1 cm^3 were taken for oil analysis. These samples were composed primarily of zooplankton, but necessarily included particulate matter, water and some phytoplankton. Oil present was extracted using 5 mls of spec-grade *n*-hexane. The hexane supernatant was analyzed on a Farrand Mark 1 Fluorescence Spectrophotometer, using synchronous-scanning techniques. The techniques, previously described by Gordon and Keiser (1974, 1976), involve scanning both excitation and emission monochromators simultaneously with a constant offset ($\Delta\lambda$) between them, in this case 25 nm. Quantitative estimates of oil concentrations present in the zooplankton samples were made by comparing their spectra with those of *Argo Merchant* standards. Because of its sensitivity and speed, fluorescence spectroscopy is generally recognized as a reliable method for monitoring oil in the marine environment.

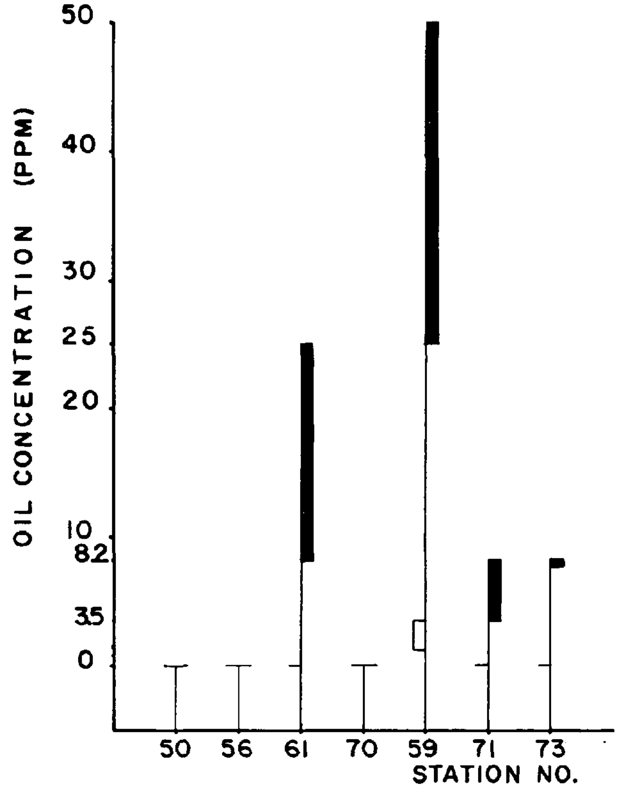

Figure 3. *Comparison of oil concentrations in plankton vs. net, .333 mm mesh.*

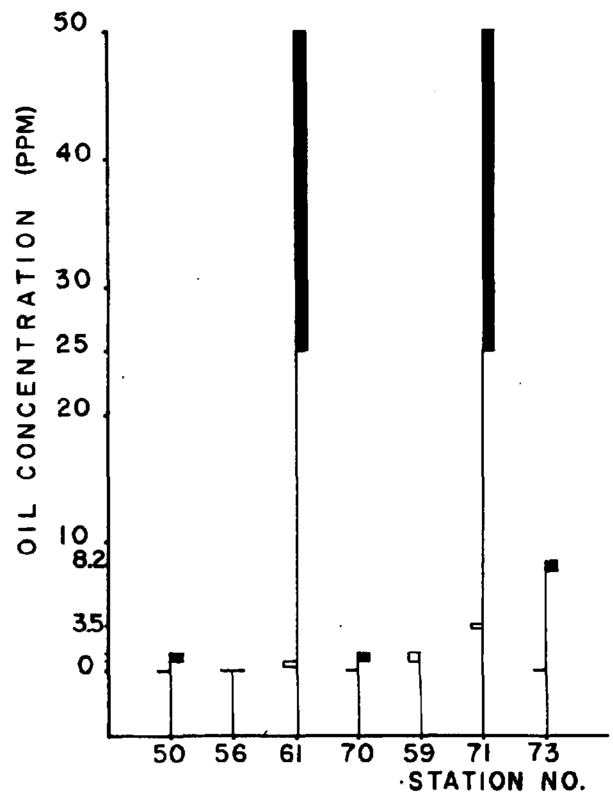

Figure 4. *Comparison of oil concentrations in plankton vs. net, .505 mm mesh.*

Table 1. Summary of Stations Sampled and Analyses Performed.
Oil concentrations in ppm.

★ indicates presence of lighter oil
+ indicates samples which were examined histologically
- indicates no oil was found
blank indicates analysis was not performed

	February 1977				July 1977		December 1977	
Station	*Mesh No.*	*Fresh*	*Frozen*	*Histo.*	*Frozen*	*Histo.*	*Frozen*	*Histo.*
44	0	-	-				-	
45	0	-	-				<.24	
47	0	1.2-3.5	-	+		+	-	
48	0	-						
49	0	-				+		
50	6	3.5-8.2		+		+		
	0	1.2	-					
57	0	75-100		+				
64	6	★						
	0	-						
61	6	.4-1.2	-					
	0	<.24	-					
62	6	★	-					
	0	★	-	+				
54	6	5-7.5	16-25					
	0	3.5		+				
56	6	25-50					-	
	0	.24-.72		+				
53	6	>117	-					
	0	>117						
52	0	.72-1.2						
63	6	25-50	>117					
	0	50-75	2.7-8.3					
58	6	8.2-25	7.2					
	0	8.2-25		+				
56	333	★						
	505	★						
61	333	8.2-25		+		+		
	505	25-50						
70	333	★		+				
	505	.72-1.2						
59	333	25-50			-	+		
71	333	3.5-8.2		+				
	505	25-50						
73	333	8.2		+				
	505	8.2						
E1				+		+		
Control	333	-	-	+				
	505	-	-					
72	505	-	-			+		

Duplicates of most samples were preserved for later examination. These were stored in *n*-hexane-cleaned dark glass bottles and frozen immediately to avoid microbial degradation of any oil present.

Zooplankton prepared for light histology were fixed in 10% buffered formaldehyde, 3% gluteraldehyde or 1% osmium tetroxide. Tissues were dehydrated in alcohol and xylene, embedded in paraffin, sectioned at 6 micrometers and stained with hematoxylin and eosin.

Externally fouled organisms were also examined with a fluorescence microscope to which a Farrand Microscope Spectrum Analyzer was attached. The organisms were examined visually, and fluorescent spectra were analyzed using 366 nm as the excitation wavelength and scanning the emitted light from 400 to 750 nm. Samples of known *Argo Merchant* oil were examined as standards. This method had previously been used to identify and quantitate crude oil taken up by protozoans (Lanier, 1977).

Results

Figure 2 charts the locations of the stations sampled. The results of chemical (UV) and histological

Table 2. Comparison of Oil Concentrations in Plankton vs. Nets.
- indicates no oil was found

Station	Date	Plankton Mesh No.	Plankton Oil (ppm)	Nets Oil (ppm)
50	26/2/77	333	-	-
		505	.72-1.2	-
56	26/2/77	333	-	-
		505	-	-
61	26/2/77	333	8.2-25	-
		505	25-50	.24-.72
70	26/2/77	333	-	-
		505	.72-1.2	-
59	26/2/77	333	25-50	1.2-3.5
		505		.72-1.2
71	27/2/77	333	.35-8.2	-
		505	25-50	3.5
73	27/2/77	333	8.2	-
		505	8.2	-

Table 3. % Contamination of Organisms Found in Formalin Preserved Samples.

Station	% Fouled Organisms	Oil Level in Fresh Samples (ppm)
73	5	8.2
62	0	0
57	4	75-100
71	25	25-50
70	2	.72-1.2
61	36	8.2-25

examination of fresh and frozen samples taken in February, July and December are presented in Table 1. It should be noted that oil concentrations observed in fresh February samples ranged from less than 0.24 ppm to greater than 117 ppm in 14 of the 22 stations sampled. The single July sample showed no trace of *Argo* oil, while one of the four samples from December did show a low concentration of *Argo Merchant* oil. The sites selected for December, however, were the least contaminated of the stations sampled in February. At some stations, indicated by an asterisk in Table 1, we detected the presence of light oil.

The possibility that these data were the result of cumulative contamination of the nets was investigated. After several tows were taken with number 0 and 6 nets, we changed to clean bongo nets of comparable mesh size. Strips of netting of the same material and mesh size were attached in the caudal end of the new nets. After each tow, a swatch was taken from these strips and analyzed for presence of oil. The results of chemical analysis of net versus zooplankton are summarized in Table 2 and Figures 3 and 4. The stations are listed in the chronological order in which they were sampled. Cumulative contamination would be seen as an increasing concentration of oil on the nets from station to station. Ten of the fourteen net swatches showed no *Argo* oil present. At those stations where net contamination was apparent,

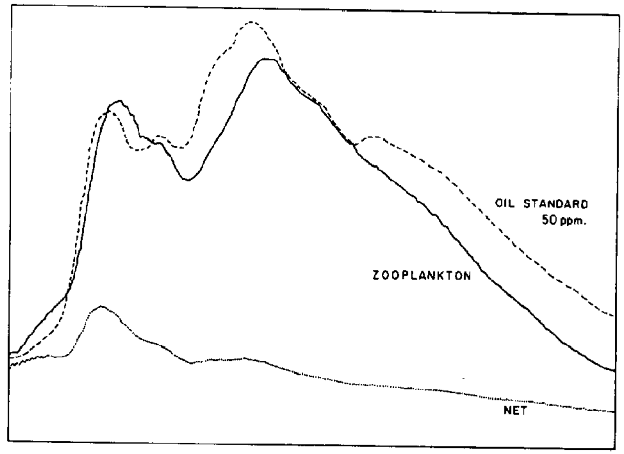

Figure 5. *Fluorescence spectra of hexane extracts of net material and zooplankton compared with Argo Merchant oil standard.*

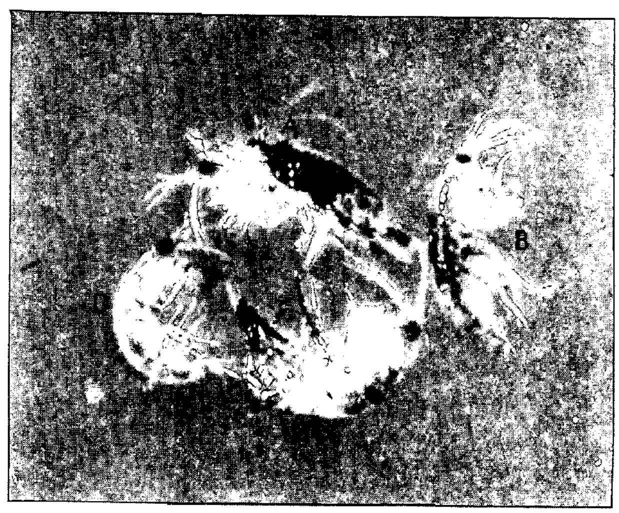

Figure 6. *Gammarid amphipods showing varying contamination, external and internal, as well as clean amphipods.*

the concentrations of oil associated with the net material were 8 to 100 fold less than that associated with the net content. Figure 5 compares spectrofluorometric tracings of the hexane extracts of net material and zooplankton, with a known standard of *Argo Merchant* oil.

Histological examination of both fresh and fixed samples revealed that some zooplankters were contaminated with oil. The amphipods in Figure 6 illustrate the types of fouling of the zooplankton. Amphipods A and C had externally-fouled carapaces. Amphipod B appears to have internal contamination, while amphipod D is apparently clean. When formalin-preserved zooplankton samples were examined nine months later, oil could still be observed on and in the animals. At five stations with samples showing contamination in February, the incidence of fouled individuals varied from 1 to 25% of the total sample (Table 3). To establish the nature of the fouling material, a sample of several contaminated organisms from the 5 stations were mascerated and extracted in hexane. A synchronous-scanning spectro-

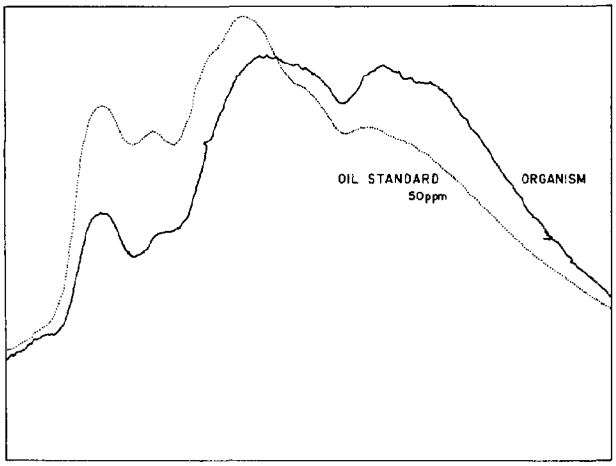

Figure 7. *Fluorescence spectra of hexane extracts of 6 organisms preserved in formalin compared to the fluorescence spectra of an Argo Merchant oil standard.*

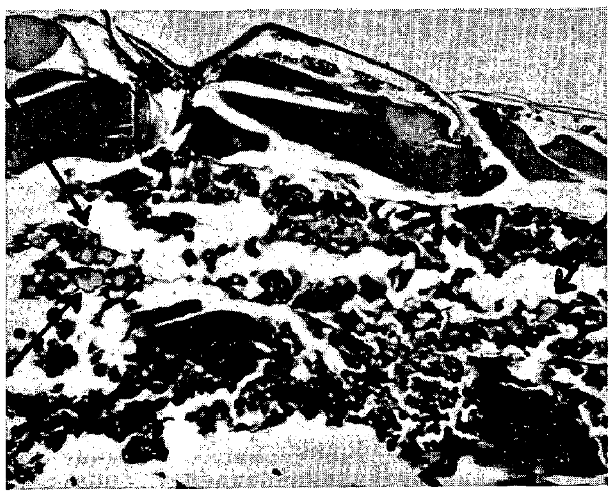

Figure 8. *Longitudinal section of a fouled copepod from station 56, showing globules of an oil-like material. (Mag. 10x.)*

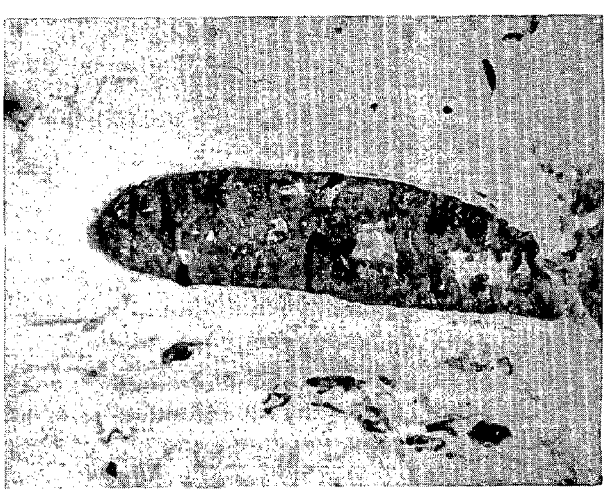

Figure 9. *Longitudinal section of a "clean" copepod, from station 73, without globules of oil-like material. (Mag. 10x.)*

fluorometric analysis of the hexane extract is shown in Figure 7, and compared with an *Argo Merchant* oil standard.

The organisms were also examined using fluorescence microscopy and a microscope spectrum analyzer. *Argo Merchant* oil standards, however, emitted no measurable fluorescence spectrum when excited at 366 nm and scanned from 400 to 750 nm. Visual examination of the fouled organisms using fluorescence microscopy revealed the entire organism fluorescing with the exception of the black globules suspected of being *Argo Merchant* oil.

Histopathological examination of the osmium fixed specimens collected in February showed that an oil-like material was present not only on the external surfaces of the animals but also in the area of the gut (Figure 8). Neither the zooplankton specimens collected from the February control stations nor the July specimens showed a comparable oil-like material in the gut or on the carapace (Figure 9).

Discussion

Estimates of oil concentrations in the water column vary with station, time and the mesh-size of the net. The variation from station to station in February can be seen in Table 2. The same station, when sampled on 2 days, using the same mesh-size, yielded different results. The station 61 sample, on February 23, had an oil concentration of less than 0.24 ppm, while on February 26 the same sample from the same mesh-size net had an oil concentration of 25-50 ppm. Different concentrations were obtained from the 2 mesh sizes used at the same station on the same day. At station 56 on February 24, the #0 net yielded a concentration of 0.24-0.72 ppm while the #6 net had a concentration of 25-50 ppm. This variability in the observed concentrations appears typical of the uneven distribution of oil in the surface water, the water column, sediments, beaches, organisms and tissues. Because of this uneven distribution, large numbers of samples are essential to assess the degree of contamination of an area or of organisms.

Where differences in concentration were found in samples from different mesh sizes, the smaller mesh (333 mm, no. 6) generally yielded higher concentrations. This is consistent with the idea that a smaller mesh would retain more of the particulate matter found in the water column.

Argo Merchant oil concentrations as high as 117 ppm were found in the water column of the area two months after the spill. As we are dealing with a shallow and turbulent region, this high concentration may be due to the resuspension of sediments and oil into the water column, thus maintaining its availability to the zooplankton community. The dynamic nature of the shoals (high turbulence, shifting sediments and changing currents) contributes to the dispersion of oil.

Although the bulk of the oil apparently shifted from the site of the wreck, there appears to have been a gradient of decreasing oil concentration with distance from the wreck beyond this shift. The highest concentrations of oil observed were not found immediately adjacent to the wreck. For example, station 70 had an oil concentration of 0.72-1.2 ppm while station 57 had a concentration of oil of 75-100 ppm. Examination of the results for the south-west transect, shown in Figure 2, indicates the presence of a gradient. Station 73 had a concentration of 8.2 ppm; station 50: 3.5-8.2 ppm; station 47: 1.2-3.5 ppm; station 45: 0; and station 44: 0 (Table 2).

When the frozen samples were analyzed chemically nine months after they were taken, no correlation was found between concentrations in fresh and frozen samples. This may be attributed to several factors:

a) the storage temperature may not have been low enough to inhibit microbial activity,

b) repeated thawing and freezing of material may have accelerated degradation of the oil,

c) dewaxing of oil present, during long storage.

Optimum storage temperature should be -30°C, and the maximum storage period should be less than 2 months (Engelhart, 1977). The weathering of oil standards stored along with the samples should be investigated for comparison.

Formaldehyde preservation apparently does not greatly affect the fluorescence spectrum of oil. Fouled organisms preserved in formaldehyde yielded spectra similar to that of *Argo Merchant* oil, when extracted with *n*-hexane and observed with the synchronous-scanning fluorescence spectrophotometer. Whether the concentration of oil remains unchanged through time remains to be explored.

The total oil present in our samples is most likely due to combinations of the following factors:

1) oil in the gut
2) oil in body tissues
3) water soluble fractions
4) adhering emulsions of oil and tar.

Oil in the gut may be due to oil coated material or oil particles that are directly ingested by zooplankton. Parker et al. (1971) demonstrated the presence of "considerable quantities" of oil in the guts of copepods and barnacle larvae after exposing them to a fine suspension of oil of 2-10 ppm for 18 hours at 10°C. Conover (1971) reported zooplankton ingesting oil droplets of Bunker C after the *Arrow* spill. The oil had no observable effect on the organisms and apparently passed through the intestines essentially unchanged. Histological examination of our February samples indicated oil-like droplets in the guts of the copepods and amphipods collected from heavily contaminated areas of station 56.

Oil may be transferred from the gut to the body tissues. Oil may also reach the body tissues by uptake through other body surfaces. Lee (1975) described the uptake, metabolism, storage and discharge of petroleum hydrocarbons by selected marine zooplankton and benthos. Both paraffinic and polycyclic aromatic hydrocarbons were added to seawater containing various species of zooplankton collected off California, British Columbia and in the Arctic, including the copepods *Calanus plumchrus, C. hyperboreus, C. helgolandicus* and the amphipod *Parathemisto pacifica.* The uptake of dissolved hydrocarbons was linear for 24 hours, with no further increase in stored hydrocarbons after that time. Most ingested hydrocarbons were metabolized and discharged by the various crustacean species, although a small percentage (less than 1% of ingested hydrocarbons) was retained by all species even after a "long depuration time". The above phenomenon was also observed by Morris (1974) in the field. He found high levels of hydrocarbons in the lipids of near surface samples of zooplankton of the eastern Mediterranean. Thin layer chromatography showed a complex mixture of hydrocarbons similar to that present in petroleum and found in the emulsion and surface film samples of the area. The field study suggested that the species of zooplankton investigated can store and concentrate pollutant hydrocarbons which were present in the surface waters.

Stegeman (1977) points out that the metabolism of certain petroleum hydrocarbons, which may be relatively inert, can result in the production of highly toxic and carcinogenic derivatives.

A component of the observed concentrations may be due to the fractions of oil dissolved in sea water. The amount of water soluble fractions seems to vary depending on the oil involved. Anderson et al. (1974) examined water soluble fractions of No. 2 fuel oil, Bunker C residual oil, Kuwait crude and South Louisiana crude. The two crude oils gave more concentrated water soluble fractions than did the two refined oils. Frankenfeld (1973) investigated the weathering of No. 2 fuel, Bunker C and Venezuelan crude under simulated natural conditions. After a week of weathering in laboratory simulators, the dissolved fractions of No. 2 were approximately 3.5 times those found for the heavier oil. After one month, 1.4 ppm of Louisiana crude and 3 ppm of No. 2 fuel remained in solution. This finding disputes reports that light oils disappear almost entirely due to evaporation shortly after being introduced in the marine environment.

Because of the turbulent conditions in the area of the *Argo Merchant* wreck, some component of the oil concentrations observed may be due to adhering emulsions of oil and tar. If a relatively thick oil film undergoes violent agitation at the air-sea interface, even gasoline may form a temporary emulsion (Blackman et al., 1973). Rough seas tend to create emulsions of the oil in water phase. Berridge et al. (1968) studied the formation and stability of water in oil emulsions and found that they were stable for periods exceeding 100 days. According to Berridge, water in oil emulsions do not require the addition of external dispersing agents but form naturally on a dynamic sea surface.

Small tar balls were noted during the examination of the material. These could be the cause of the external fouling of the carapaces. It is conceivable that a residual tar ball is responsible for the presence of oil at station 45 in December 1977 (less than 0.24 ppm). However, the fraction indicated by the spectrum is lighter than that normally found in tar balls.

Conclusions

The study indicated that spectrofluorometric analysis of zooplankton samples can be used to determine the geograhic extent of oil in the water column and the persistence of oil residues following an oil spill. Fluorescence spectroscopy allows for an almost positive identification of the oil involved, as well as preliminary quantitative assessment of the oil levels, provided that spectra of the oil standards are available.

This method was used to detect *Argo Merchant* oil in the water column in the area of the wreck two months after the spill and, in one case, twelve months after the spill. Some of this oil was associated with zooplankton. The oil was observed adhering to the carapaces of zooplankton and apparently ingested by the organisms.

Samples preserved for several months in formaldehyde contained identifiable *Argo Merchant* oil, indicating that formaldehyde may be an acceptable oil preservative for spectrofluorometric analysis through further investigation is necessary.

It was not possible to identify the oil-like globules in the guts of crustacean zooplankton using fluorescence microscopy, although this technique may be useful for oils with higher concentrations of aromatic fractions.

Although these techniques demonstrate the presence of oil, in order to detect the effects of persistent low level petroleum concentrations in the marine environment, studies of the effects on zooplankton of water soluble fractions, oil contamination of food, plants and lower trophic levels should accompany field observations.

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Field and Laboratory Measurements of Stress Responses at the Chromosome and Cell Levels in Planktonic Fish Eggs and the Oil Problem

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Abstract

Abnormalities in chromosome makeup at the early embryo stage may be at least one of the most sensitive practical indicators of the sublethal effects of marine pollutants on reproduction in fish. Cytogenetics - the study of chromosomes and their divisions as they affect heredity - has been applied to fish rarely in the past. It is only recently that reliable methodology has been developed for conducting cytological and cytogenetic studies on fish eggs from plankton samples taken at sea. These methods are even more easily applied to cytological-cytogenetic analyses of fish eggs used in laboratory experimentation on oil and other contaminants. This methodology, first developed and used in conjunction with a study of the eggs of Atlantic mackerel, *Scomber scombrus,* in the New York Bight, is described.

Using the same procedures as for mackerel eggs, microscopic examinations were made of the dissected embryos of 79 cod and 162 pollock eggs taken from surface waters in the vicinity of the *Argo Merchant* spill. Seventy-five cod embryos from eggs of a laboratory spawning of aquarium-held fish were also examined. This study was greatly limited by the small number of eggs available. Cod and pollock eggs were scarce at the cleaner stations. This made precise station and species comparisons impossible, though some could be made, using the combined estimates of cytological mortality and cytogenetic moribundity.

Eggs at all stations showed some oil contamination of the chorion, although fewer cod than pollock eggs were fouled. A higher mortality of pollock eggs was also apparent. Overall, about 20% of the cod eggs were dead or moribund, compared with 46% of the pollock eggs. However, only 4% of the laboratory-spawned cod eggs were dead or moribund.

At a station within the oil slick, pollock embryos were grossly malformed in 18% of the eggs, and at the periphery of the slick, 9% were grossly abnormal. No embryos of cod showed abnormalities, nor were there any abnormal pollock embryos at any stations more distant from the slick.

Introduction

When fish eggs are spawned at sea they are arrested at the metaphase or telophase stage of the second meiotic division of their chromosomes. On fertilization they

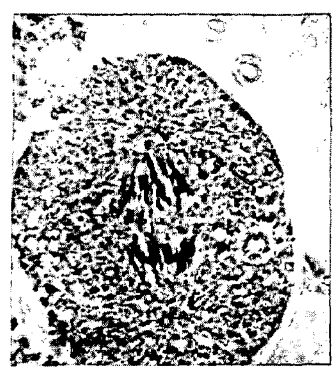

Figure 1. *Just before the 2-cell Atlantic mackerel embryo of Fig. 2 was formed, it underwent its first mitotic division, as seen in this photomicrograph of mackerel cleavage.*

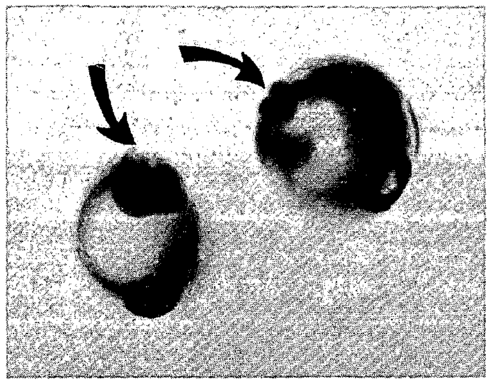

Figure 2. *Pelagic Atlantic mackerel eggs as they occur in surface waters. Egg to the left has completed its first cleavage division and has a 2-cell embryo (see arrow). Body to bottom of the egg is the oil globule characteristic of some species eggs. Egg to the right has a 4-cell embryo at arrow. Actual egg size about 1 mm. As viewed under low magnification with dissecting microscope.*

complete this genetic-sensitive division. The well-established genetic vulnerability of gametogenesis is further increased as the fertilized egg enters early cleavage (Figure 1) (Solberg, 1938; Muller, 1959; Murakami, 1971). The genetic vulnerability of fish eggs to induced mutation appears second only to the most sensitive mammalian egg (Donaldson and Foster, 1957; Polikarpov, 1966; Purdom and Woodhead, 1973). Aquatic environmentalists who investigate contaminant effects on reproduction via non-genetic approaches conclude that reproduction seems to be one of the most sensitive measures of chronic sublethal effects clearly meaningful in nature (Sprague, 1971; Rosenthal and Alderdice, 1976).

Many of the important commercial species of fish have planktonic eggs that develop in the upper portion of the water column, often at the air-water interface (Figure 2). Not only is the ocean surface microlayer directly exposed to atmospheric pollutants, it also appears to concentrate heavy metals and chlorinated and petroleum hydrocarbons (Duce et al., 1972; MacIntyre, 1974). It bears the brunt of oil spills. As immobile occupants of surface waters, buoyant fish eggs will inevitably be exposed to whatever noxious components escape from oil slicks and oil droplets in this vicinity. There is some evidence that fish may actively avoid oil spills. However, eggs can drift into spills, and choice of alternate spawning beds could result in poor development because of unfavorable or less than optimal natural environmental conditions of these other grounds. Further, spills may occur after spawning, while embryo development is already under way, as in the case of the *Argo Merchant.*

The low-boiling-point aromatic hydrocarbons of oil are soluble in water. They also are highly soluble in lipid material, as present in fish eggs. Benzene, the most abundant such chemical compound in crude oil, has proved mutagenic in a number of tests on different organisms. Polynuclear aromatic hydrocarbons can act as both carcinogens and mutagens (Hollaender, 1971a and b). At least when No. 2 oil is exposed to irradiance as it would receive from sunlight, photooxidation produces compounds more toxic and persistent, and more water soluble than those present before irradiation (Scheier and Gominger, 1976; Larson et al., 1977). Peroxides produced by this process can form free radicals which react with the hereditary DNA to produce mutations. On photooxidation, other toxic components already present, such as phenols, increase over a period of days. Phenols can be mild chromosome-breaking agents (Hollaender, 1971a and b).

Certainly, the membranes and jelly coat of fish eggs afford some considerable measure of protection against pollutants and, once hatched, larvae may exhibit increased physiological sensitivity to some pollutants. Such protection though is most likely temporarily diminished when perivitelline fluid formation takes place after fertilization and the pollutant enters the egg with imbibed water. A pollutant which damages or disorganizes the egg membranes will modify their permeability. Aromatic compounds of oil appear to alter the surface properties of cell membranes, as studied by the spin-labeling technique, while paraffin hydrocarbons do not (Roubal and Collier, 1975). However, studies specifically on the membranes of fish eggs have not been conducted.

The sensitivity of the early embryo stages of any species to chromosome damaging mutagens, and to cytotoxins which can disrupt the orderly division of the chromosomes, lies, in large measure, in the necessity of the embryo for a normal complement of unaltered chromosomes for normal development to proceed (Sonnenblick, 1940; Whiting, 1945; Muller, 1954a and b; Cave and Brown, 1957; von Borstel and Rekemeyer, 1959; von Borstel, 1960; Epstein et al., 1970; Bateman and Epstein, 1971). Some measure of natural, background gametic wastage in fish could be the result of such natural environmental variables as light, temperature, salinity and oxygen acting on the highly sensitive meiotic and early egg stages. Chromosome errors are almost invariably lethal if they occur before the gastrula stage. Unlike physiological effects, there can be no recovery. After gastrulation of the embryo, lethality will depend on the number of affected cells and the destiny of their cell lineages in development. The correlation with lethality, however, remains strong. Mutations occurring during the period of major organogenesis lead to developmental abnormalities of systems not fully developed in fish until the post-hatching period.

Generally, genetics has thus far had little impact on fishery biology. Similarly, fish have played only a minor role in the development of genetics. The value of any kind of genetic monitoring of fish has not hitherto been considered by groups addressing marine baseline and monitoring approaches (Longwell, 1975; McIntyre, 1976). Still, in a review of measurement of pollutant toxicity to fish, Sprague (1971) comments that tests for reproductive damage are rightfully regarded as the most important in determining "safe" concentrations.

The explosion of interest in vertebrate cytogenetics, that is, the study of chromosomes as they affect heredity of the cell, the individual and population, was confined to mammals. Fish were largely by-passed even though they comprise the largest of all vertebrate groups. Roberts (1967) reviewed the status of chromosome cytology of the Osteichthyes. Investigating the effects of incorporated radionuclides, the Russians more than any other group have conducted experimental cytogenetic studies on fish eggs (AEC-TR-6940, 1968; AEC-TR-7418, 1971; AEC-TR-7299, 1972). Although Polikarpov (1966) notes the importance of direct studies on the neuston, the richest biosphere in the world, these Russian studies were still limited to the spawn of experimental, laboratory-treated fish.

In 1974 a cruise of the sailing vessel *Westward* of SEA (Sailing Education Association) provided a large collection of Atlantic mackerel *(Scomber scombrus)* eggs from 40 stations over the variously polluted New York Bight. Using this egg collection, appropriate methodology was developed for cytogenetic study of fish eggs collected at sea in plankton samples. This methodology was then applied to a study of these eggs. First efforts in this regard and methods were described in a NOAA Technical Memorandum (Longwell, 1976). Since then, more than 15,000 eggs, mostly from plankton samples, have been processed and examined cytogenetically. Most of these have been mackerel.* However, about a dozen other species, demersal and planktonic, have also been processed, enough to establish that just about any species of egg might be so studied.** Results of mackerel work and improved methodology are now being prepared for publication in a NOAA Technical Memorandum and elsewhere.

Procedures for Cytogenetic and Cytological Study of Fish Embryos. Plankton samples are collected at sea with either neuston or bongo nets towed at appropriate levels of the water column similar to standard tows for assessing zooplankton. Tow time and speed are adjusted to minimize any damage to fish eggs. Efforts are made to estimate water flow over the eggs in the tow process. Immediately on being brought aboard the vessel, plankton is fixed in a 1:10 dilution of buffered histological grade formalin. At-sea physical factors that could affect egg viability, such as temperature and salinity, are measured at each sample station.

Once fish eggs are picked out of the fixed plankton in the laboratory, they are identified to genus and species. They are then sorted by developmental stage. Eggs at each developmental stage are carefully scrutinized under low magnification to appraise overall egg and embryo condition. At this time abnormalities of gross development are noted.

Under a low-power microscope, the embryo is dissected from the egg with a needle (Figures 3 and 4). After post-fixation in acetic acid, the fragile embryo is stained and squashed into a monolayer of cells on a microscope slide (Figures 5 and 6). For cytogenetic work, the staining medium is the standard aceto-orcein to which proprionic acid is added. Cells and their dividing chromosomes are viewed under high-resolution, high-power, light microscope optics.

Depending on developmental stage, the fish embryos lend themselves more or less well to the collection of different kinds of data on their chromosomes and mitoses (to be described fully in a forthcoming NOAA Technical Memorandum).

In mackerel from the New York Bight a large percentage of observed early cleavage embryos was dividing irregularly at the chromosome level or showed

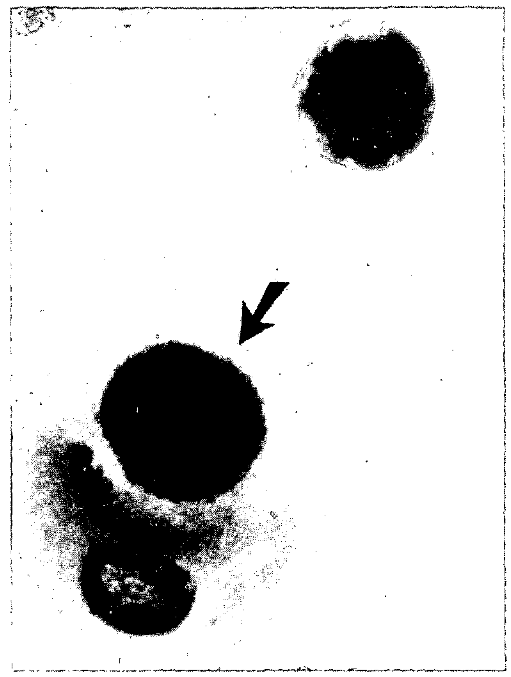

Figure 3. *Planktonic Atlantic mackerel egg at very early morula stage of development, and embryo dissected off its egg. Arrow points to embryo still in the egg. Characteristic oil droplet is to bottom of the egg. Body to upper right is morula-stage embryo dissected off its egg in preparation for examination of its cells and chromosome divisions. Actual egg size about 1 mm. As viewed under low magnification with a dissecting microscope.*

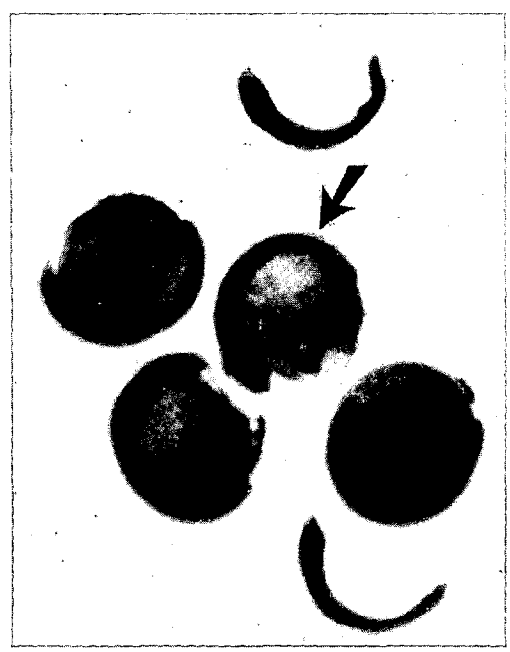

Figure 4. *Planktonic Atlantic mackerel eggs at the later tail-free stage of embryo development - the stage of a large portion of the pollock eggs sampled at the time of the Argo Merchant spill. Arrow points to a tail-free embryo partly encircling its eggs. At top and at bottom of the photomicrograph are two such embryos dissected off their eggs. Actual egg size about 1 mm. As viewed under low magnification with dissecting microscope.*

*Mackerel studies and methods development have been supported by the Marine Ecosystems Analysis Program of NOAA.

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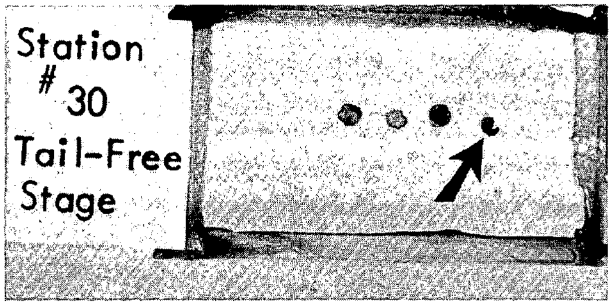


Figure 5. *Four tail-free embryos dissected off planktonic fish eggs squashed onto microscope slide, stained, and ready for study of their cells and mitotic divisions. Near actual size.*

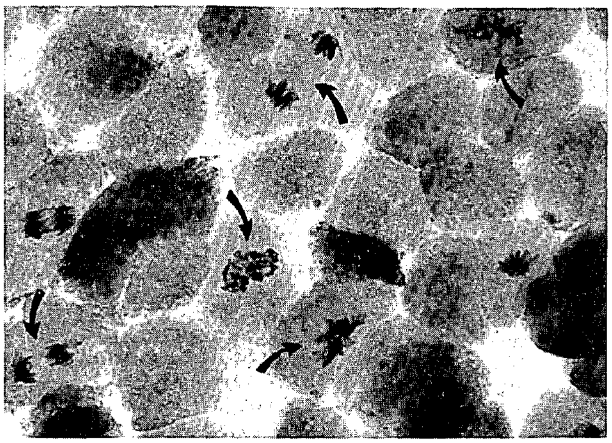


Figure 6. *Monolayer of gastrular cells of whiting (Merluccius bilinearis) embryo prepared for cytological-cytogenetic study. Several normal mitotic configurations are obvious. Light microscope, 63 X objective.*

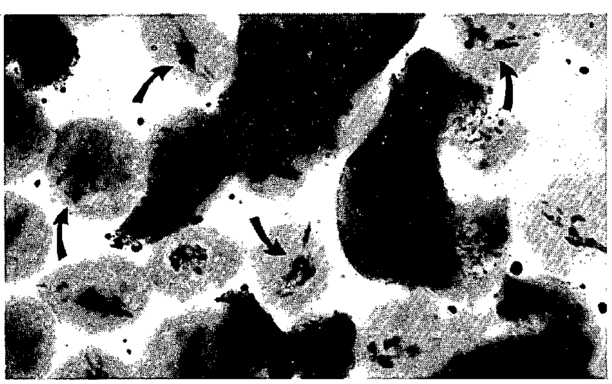


Figure 7. *Monolayer of gastrular cells of whiting (Merluccius bilinearis) embryo with abnormal chromosome configurations unable to complete their mitoses. Light microscope, 63 X objective.*

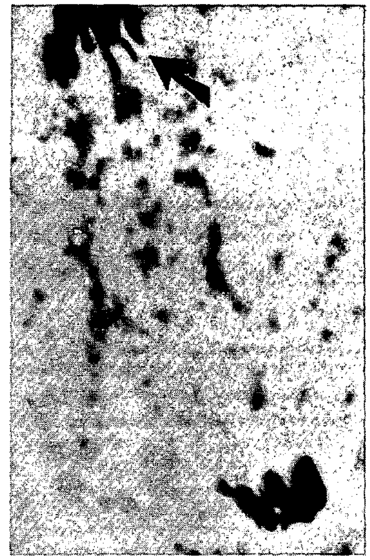
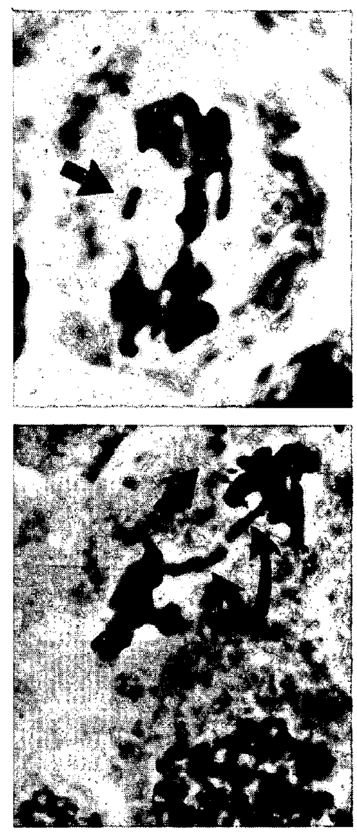


Figure 8. *Normal mitotic telophase at gastrula stage in mackerel embryo from a planktonic egg. Arrows point to one of the two daughter groups of just divided chromosomes. Light microscope, 100 X objective.*



Figures 9 and 10. *Two abnormal mitotic telophases at gastrula stage from planktonic mackerel eggs. Note chromosomes lagging between, and bridging the two groups of daughter chromosomes and to the back of one group. Such telophase irregularities are indicative of chromosome damage, and result in irregular distribution of chromosome material to daughter cells. Light microscope, 100 X objective.*

Figure 11. *Grossly abnormal mitotic telophase in mackerel embryo from a planktonic egg. Extremely abnormal stickiness of the chromosomes has caused them to lose their distinctness and prevents their completing this mitotic division. Light microscope, 100 X objective.*

Figure 12. *Chromosomes from a tail-bud Atlantic mackerel egg picked out of a routine plankton sample. For karyotyping chromosomes, animal and plant cells are usually pre-treated with colchicine before fixation, but this may not be necessary for most work on these fish eggs. The egg involved here was not treated with colchicine. Light microscope, 100 X objective.*

early signs of cell death or nuclear lysis. Often the mitoses essential to continued development had ceased altogether. Any of the ensuing developmental stages might also show division arrest. At the subsequent blastula and gastrula stages mitotic telophase configurations are good indicators of the regularity of chromosome division, and of cytotoxic effects on the chromosomes and translocation of broken chromosomes that lead to chromosome bridging. Blastular and less often gastrular embryos with totally disorganized mitoses in nearly all their cells are not uncommon (Figure 7). At the gastrular stage abnormalities of the mitoses drop dramatically, most abnormal embryos being unable to gastrulate. Unlike earlier stages, which

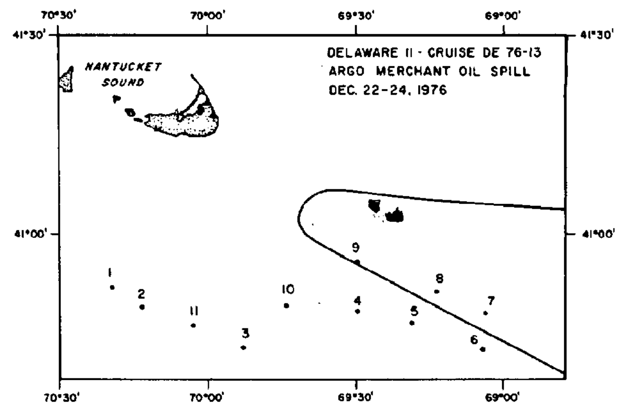


Figure 13. *Station locations for Delaware II cruise. The solid line indicates oiled area.*

differ widely in number of mitoses partly because of wide variation in cell number, the number of mitoses in gastrulating embryos is readily recognizable as an indicator of embryo well-being. The chromosome configurations in the tail-bud and tail-free stages become smaller, but telophase bridging is still readily scorable. Mitotic index remains a good indicator of embryo condition throughout embryo development once influencing factors like temperature are taken into consideration. See Figures 8-11.

As development proceeds, characteristic patterns of cell differentiation appear in the various stage embryos. Aberrations of some of these patterns, a portion of which is no doubt related to abnormal chromosome events, are readily discernible even in monolayered preparations. Most common among these are: abnormally, prematurely differentiated nuclei in blastular and gastrular embryos, often with too many cells of too small size; the retention of one or more large, undivided early-cleavage cells in otherwise later-stage embryos; and the dramatic de-differentiation of the cells of the early or later-stage embryos. All of these phenomena are readily observable in the course of examining embryo mitoses, and records are kept on such observations.

A recent methods development at the Milford laboratory has made it possible to characterize individual chromosomes of the planktonic fish eggs using their yolk-sac membranes and also the meiotic configurations of prespawned eggs stripped from fish in the field (in preparation for publication). It is now possible to detect induced abnormalities of chromosome numbers and form, as was done on mammalian cells in laboratory tissue culture and to do this on field collections of fish eggs. See Figure 12.

All of this methodology is, of course, applicable to fish eggs utilized in laboratory experiments.

The *Argo Merchant* Study

Field Sampling of Fish Eggs in the Argo Merchant Spill. A portion of the eggs from the ichthyoplankton samples taken during the Northeast Fisheries Center's *Delaware II* December 22-24 cruise to the site of the *Argo Merchant* spill (Figure 13) was sent to the Milford laboratory for microscopic study of their embryos. Plankton was collected at cruise Stations 4-9 with standard oblique tows of the water column with bongo nets, and of the water surface with neuston nets. No tar-like surface oil was

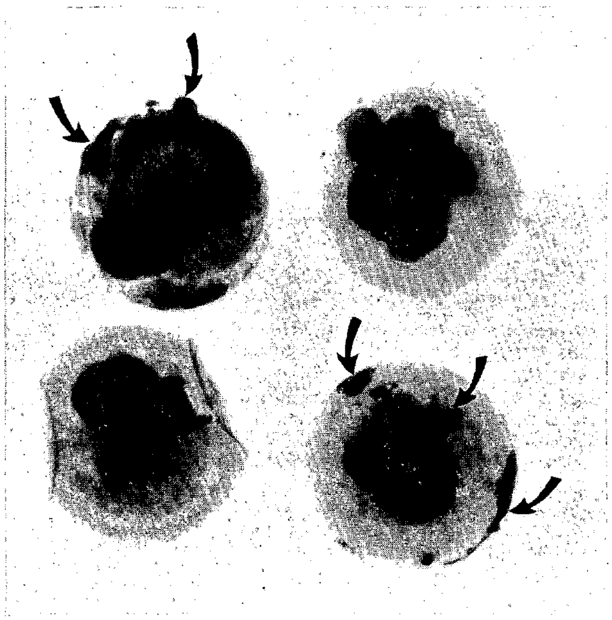


Figure 14. *Pollock eggs sampled at edge of the Argo Merchant oil slick. Tail-bud and tail-free embryo stages. Egg at upper left and egg at lower right have their outer membrane contaminated with a tar-like oil. Arrows point to some of the oil masses. The uncontaminated egg at upper right has a malformed embryo. The uncontaminated egg at lower left is collapsed and also has an abnormal embryo. Actual size of pollock eggs around 1 mm; of cod eggs around 1.5 mm.*

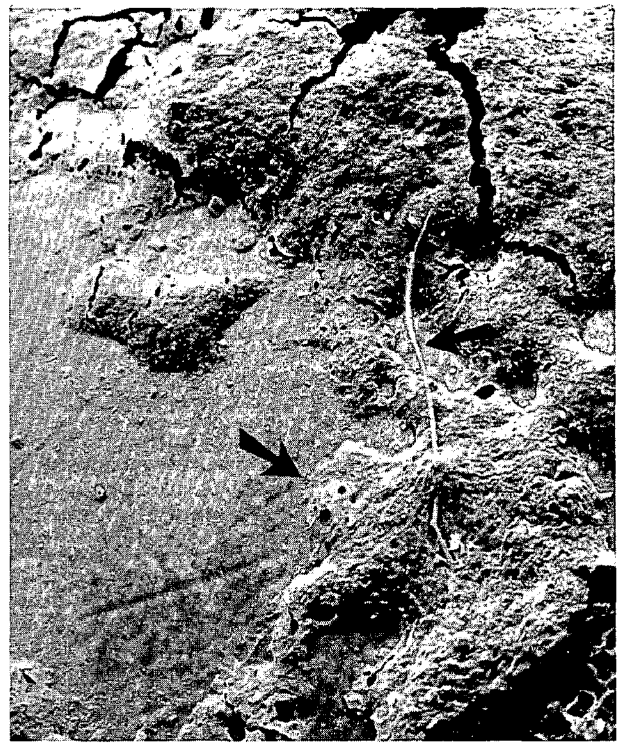


Figure 15. *Surface of an oil-contaminated pollock egg from edge of the Argo Merchant slick. Arrow at left points to one clump of oil. A clean portion of the outer egg membrane, its pores barely visible at this magnification, shows to the left, above and below this arrow. Arrow on right points to an antenna of a copepod stuck in a mass of the oil adhering to egg membrane. Copepods are other components of surface waters observed to be fouled with Argo Merchant oil. Scanning electron micrograph. About 500 X.*

observed at cruise Stations 4, 5, or 6, and the bongo net samples of the water column were clean. Samples taken at the surface with the neuston nets, however, contained specks of tar. Stations 7 and 8 were thick "pancake"-like oil slicks that resembled wrinkled black cloth floating on the water surface, and the neuston nets became saturated with oil. No fish eggs were collected at Station 7. Station 9 was at the periphery of the thick slick. This station had extremely high numbers of zooplankton and total biomass. Eggs and "pancakes" alike must have changed locations prior to the sampling but, presumably, not to such a degree as to nullify completely the sampling strategy.

Fish eggs were examined and identified at the Narragansett laboratory and Sandy Hook laboratory of the National Marine Fisheries Service. Only cod *(Gadus morhua)* and pollock *(Pollachius virens)* eggs were present in the samples. Pollock eggs were most numerous within and adjacent to the thick floating slicks. Cod eggs occurred largely about the periphery of the spill area.

Oil Contamination of the Outer Membrane of the Fish Eggs Sampled from Surface Water. Eggs at all sample stations showed some oil contamination of their outer membrane, the chorion. Oil droplets and tar adhered to roughly half of all fish eggs examined (both species, all stations). Almost all the pollock eggs at Station 9, just outside the "pancake"-like slicks, had their outer membrane fouled with a tar-like oil (Figures 14-16). In one estimate this was 94% of 49 pollock eggs. Pollock eggs at Station 9 were all quantitatively more fouled than at other stations. The particles of oil adhering to cod eggs at this station, however, did not appear any larger, generally, than at the other stations, and fewer of the cod eggs were fouled than were the pollock (60% of 60 in one estimate). There might also have been less contamination of the cod at the other stations. Scanning electron microscopy of the cod and pollock eggs sampled from the spill vicinity reveals a different pore structure in the two species. See Figures 17 and 18.

Cytological-Cytogenetic Study of Cod and Pollock Eggs from the Argo Merchant Spill Area. Microscopic examinations were made of the dissected embryos of 79 cod and 162 pollock eggs taken from surface waters in the spill vicinity of the *Argo Merchant.* Also examined were 75 cod embryos from eggs of a laboratory spawning of aquarium-held fish at the NMFS Narragansett laboratory.

Total numbers of eggs available for study were drastically limited. Cod and pollock eggs were both infrequent at the cleaner stations (Table 1). Of the cod eggs 63% were earlier than the tail-bud stage with the very earliest stages well-represented. Pollock eggs were divided equally between the later tail-bud embryo and tail-free embryo stages. All this made precise station and species comparisons impossible. Even so, using combined estimates of cytological mortality and cytogenetic moribundity, some comparisons could be made.

Embryos which had ceased to undergo mitosis were categorized as moribund. Cod and pollock eggs in the

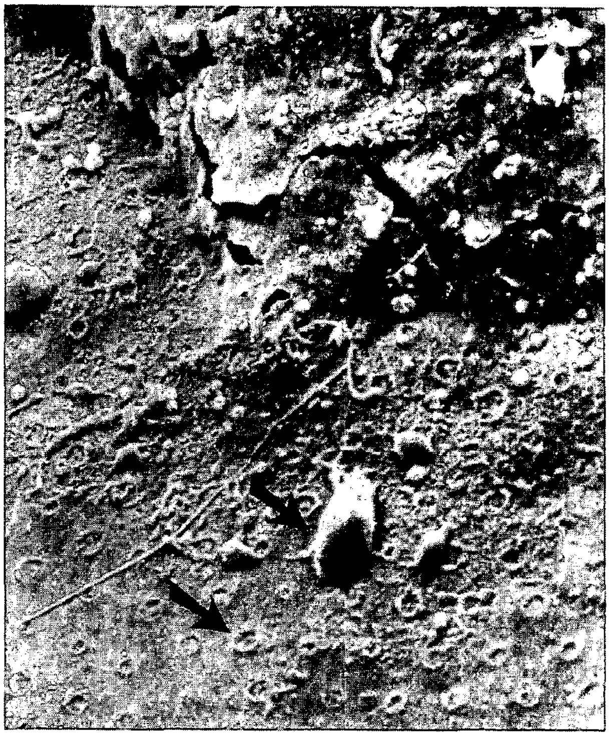


Figure 16. *Portion of surface of oil-contaminated pollock egg of Fig. 15 at greater magnification. Upper arrow points to one of many oil droplets. Lower arrow points to one of the membrane pores. Scanning electron micrograph. About 5000 X.*

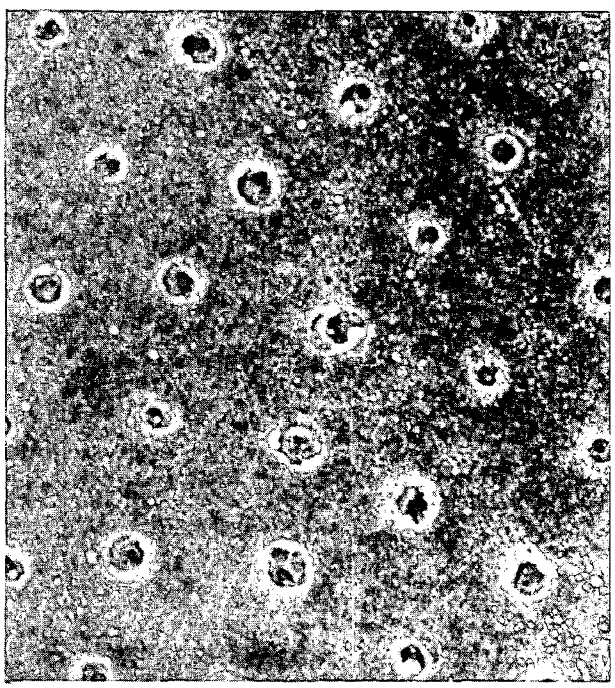


Figure 17. *Still greater magnification of a portion of surface of seemingly clean pollock egg from Argo Merchant spill vicinity, showing pore pattern of outer egg membrane, the chorion. Scanning electron micrograph. About 10,000 X.*

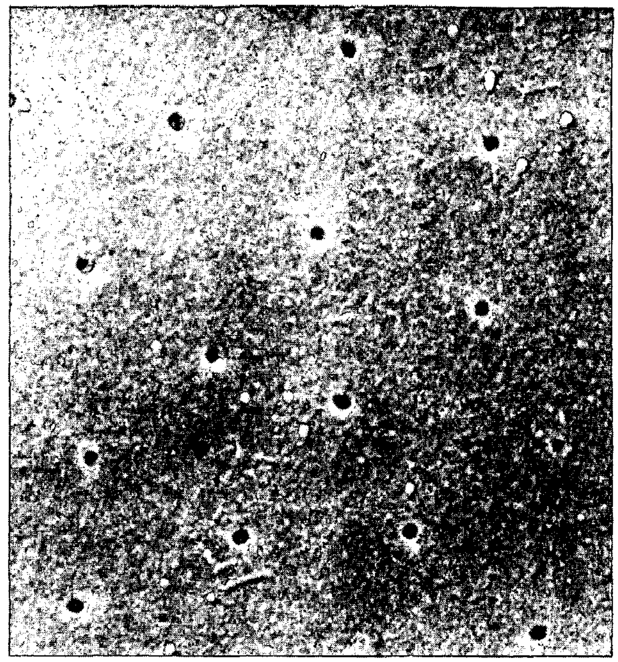


Figure 18. *Portion of surface of seemingly clean cod egg from Argo Merchant spill vicinity, showing pore pattern of outer egg membrane, the chorion. Scanning electron micrograph. About 10,000 X.*

dead and moribund categories showed a combination of cytological abnormality of the embryo's cells or of the nuclear configurations coupled with division arrest. For both the cod and pollock eggs, there was an extremely wide within-station variation in embryo mitotic index for the same developmental stage (Table 2). Many embryos still exhibiting a low number of mitoses may have been on their way to complete division arrest.

A higher mortality of pollock over cod was apparent even though the cod eggs were at earlier, more sensitive development stages at which higher natural mortality might be expected. Totaled over all the stations, about 20% of the collected cod eggs were dead or moribund, compared with 46% of the pollock eggs. As noted above, fewer cod eggs were fouled and less so than the pollock. Only 4% of the samples of cod eggs spawned in the laboratory were dead or moribund at about the same assortment of developmental stages as the samples from the vicinity of the oil spill. If this cod control is representative, then the cod were experiencing higher than usual mortality for cod in the spill vicinity but still less mortality than the pollock.

At Station 8 in the "pancake"-like slick, pollock embryos were also grossly malformed in 18% of the eggs (Figure 14). At Station 9, the periphery of the slick, gross malformations occurred in 9% of the eggs. None were observed in any of the cod embryos or in any of the pollock embryos at any of the stations more distant from the heavy slicks.

Pollock mortality was lower at Station 8 in the "pancake"-like slick than in the more membrane-contaminated eggs of Station 9 at the slick periphery. Those Station 9 embryos (15%) which had not entirely ceased to undergo cell division had very few mitoses

Table 1. Cytological-cytogenetic assays of mortality and moribundity of cod and pollock eggs from the vicinity of the oil spill

Delaware II Cruise DE 76-13 Station numbers	*Total no. eggs*	*No. eggs viable*	*No. eggs dead or moribund*	*No. eggs with malformed embryos*
Station 4				
Cod	14	13	1	0
Pollock	–	–	–	–
Station 5				
Cod	6	3	3	0
Pollock	11	0	11	0
Station 6				
Cod	3	3	0	0
Pollock	3	0	3	0
Station 8				
Cod	1	1	0	0
Pollock	105	86	19	19
Station 9				
Cod	55	43	12	0
Pollock	43	1	42	4
Laboratory spawning cod	75	72	3	0

(Table 2). Station 9 was probably in the "sheen" fed by the "pancake", which could have been more toxic than the waters just beneath the thick slick from where Station 8 eggs must have come.

The non-dividing pollock eggs of Station 9 were characterized by rather pycnotic nuclei, which had the appearance of chromosomes arrested at prometaphase of mitosis. The cells of these embryos had a clearly non-differentiated appearance resembling the cells of an earlier developmental stage more than those they were expected to contain on the basis of their more advanced developmental stage. This suggests cellular de-differentiation in response to stress.

The chromosomes of the yolk-sac membranes of these cod and pollock eggs were not examined for direct evidence of breakage as the methodology was not yet developed.

Discussion

External Fouling of the Pollock Eggs from the Argo Merchant Spill. This appears to be the first time oil droplets have been reported adhering to fish eggs, either taken from the vicinity of an oil spill or in laboratory experiments on oil toxicity. Crude oil has been reported, as adhering to most of 22 species of coral studied, causing tissue death at the sites of adherence (FAO Report, 1977). Copepods sampled on Nantucket Shoals at the same stations as the oil-contaminated cod and pollock eggs showed external mandibular and internal contamination with oil, as has been reported in the case of other major spills (see proceedings of this symposium). Contaminating oil was of the type carried by the *Argo Merchant.* Exposure of cod eggs to No. 6 fuel oil at the NMFS Narragansett laboratory, however, failed to result in any membrane contamination (W. Kühnhold, personal communication). Oil has never been observed adhering to any of thousands of other planktonic fish eggs observed at the Milford laboratory over a period of a few years, with the recent exception of Atlantic mackerel eggs at one station in slope waters off New Jersey.

Table 2. Total numbers of mitotic telophases in pollock embryos at Stations 8 and 9

Delaware II Cruise DE 76-13 Station numbers	*Telophases (actual number or estimate)*					
	0	*3-14*	*15-25*	*±50*	*±75*	*-100 - +200*
Station 8	6	7	8	27	8	28
Station 9	35	6	0	0	0	0

External fouling of the outer pelagic egg membrane, if not proved an artifact, is important. Not only could it be obvious evidence of oil exposure, but it would also increase the risk of egg mortality. Although it does not seem very probable, the likelihood that the oil was adfixed to the fish eggs (and copepod surfaces) only during the fixation-preservation in formalin should be explored in the laboratory; likewise, the possibility that real surface contamination is readily observable only after fixation of the eggs with the resultant change in their refractive index. Net contamination is another factor to consider. The net used at Station 9 was fouled collecting samples at Stations 7 and 8. This station, interestingly, was marked by the higher than usual moribundity and abnormality. It is difficult, however, to suppose that eggs readily contaminated while collecting nets were towed through the water would not also be contaminated, at least to some degree, by mixing of oil and eggs in the water column. Also, the contaminated net yielded samples at Station 8 less fouled than at Station 9. (No eggs collected at Station 7.) Another possibility is that oil becomes attached to the chorion only at certain times: on spawning of the eggs and, again, after fertilization when membrane changes occur which might make oil contamination more-or-less likely.

Heavy fouling of the Station 9 pollock eggs cannot be attributed simply to mortality and ensuing deterioration of the membranes as these eggs were almost all only in the moribund class, as opposed to other pollock eggs which were less fouled but already showing signs of cytological death.

Any real difference in membrane contamination of the cod and pollock may be related to different depths at which these fish may spawn in the water column and the rate at which their eggs rise to the surface. Of course, duration of exposure may also be a factor. The cod eggs were at an earlier stage of development than were the pollock eggs. Another factor would be the species variation in the chorion structure. The *Argo Merchant* study is the first to apply scanning electron microscopy of fish egg membranes to any investigation of this sort.

Significance of the Limited Argo Merchant Egg Study and Suggestions for the Future. Generally, little is known about the natural factors in the environment that control the mortality of fish eggs and larvae (NOAA Technical Report, 1976). This, combined with the sparse samples of fish eggs lacking a good distribution of developmental stages, with eggs of all stations oil-contaminated to some degree, makes it impossible to determine fully the significance of the cytological-cytogenetic findings on the cod and pollock eggs from the *Argo Merchant* spill. Nonetheless, the potential of such a study applied to a field catastrophe is demonstrated.

Pre-planned strategy for handling field sampling of ichthyoplankton in the event of future spills can result in more adequate samples for cytological-cytogenetic study in the event fish eggs are abundant enough. However, suitable contemporary field controls of same species fish eggs may be insufficient or unavailable. It is essential then, if field appraisals are to be made in the future, that adequate cytological-cytogenetic baseline data be collected on important commercial species. Such estimates would have to take into account the influence of variable environmental factors like temperature and salinity and of synergisms between them, as well as the ubiquitous background loads of contaminants. Essential also is an increase in the currently inadequate base of research on the development of the earliest-stage eggs of commercial fish.

It is recognizably difficult to extrapolate from laboratory data on the toxicity of oil to fish eggs and embryos to field conditions where the oil itself is affected by the environment and the environment influences the exposure the eggs receive. However, such laboratory data, as well as field samples from uncontaminated areas, are required to obtain control values for the cytogenetic indices, as well as for other biological parameters that might be measured. Both field and laboratory controls are needed because ideal conditions for such estimates can not be reasonably met for most commercial fish in either laboratory or field alone.

Effects of oil on the chromosome divisions of developing fish embryos have not been investigated in the laboratory. To some degree, damage to the fish zygotes at the chromosome and cellular levels is probably reflected in the abnormality and increased mortality of fish embryos reported on their experimental exposure to oil or oil fractions (Mironov, 1968, 1969, 1972; Kuhnhold, 1972, 1974, and in this symposium; Struhsaker et al., 1974). The genetics group at the Milford laboratory of the Northeast Fisheries Center will be collaborating with W. Kuhnhold of the University of Keil, FRG, and the Environmental Protection Agency, Narragansett Laboratory, in a joint study on the toxicity of oil to cod eggs in laboratory culture, one facet of which will be cytogenetic.

Cytogenetic examination of fish embryos could further be of use in appraisals of salinity and temperature effects on embryonic development. These data would also be useful in establishing baselines. The developing embryo is limited in its functions largely to cell and chromosome division and cell differentiation. It might be expected then that the embryo's mitoses and other cytological phenomena might, aside from appraisals of cytotoxicity and mutagenicity to its chromosomes, be useful as a gauge of the physiological well-being of the embryo and its development rate.

The combination of this new method of studying the chromosomes and mitotic-cytological development in fish eggs with the common practice of sampling ichthyoplankton at sea may well provoke a surge of interest in development and cytogenetics of fish. This interest could generate opportunities for measuring and understanding the impact of oil spills and petroleum hydrocarbons on commercially important and other fish.

Acknowledgments

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Effects of the Water Soluble Fraction of a Venezuelan Heavy Fuel Oil (No. 6) on Cod Eggs and Larvae

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Abstract

One-half, 3, and 7 day old eggs and 2, 4, and 8 day old larvae were exposed to the water soluble fraction of Bunker C oil in static tests. The initial concentrations of the test medium were 10, 100, and 500 ppb of total CCl_4-extractable hydrocarbons. The hatching success of viable larvae and the difference in 50% survival time between control and treated larvae were measured. In the same test the heart beat rates of the treated embryos were measured, and a comparison between observed beat rate reduction and viable hatch was drawn. An attempt was made to extrapolate laboratory findings to field conditions which existed at the time of the *Argo Merchant* spill.

Introduction

To date, there have been no direct observations in the field of effects of oil on embryogenesis and larval development of fish.

Estimates of oil damage to embryos and larvae have been extrapolated from laboratory tests under simulated field conditions. Although these types of experiments (e.g., determination of LC_{50}'s) are limited by the constraints of the laboratory, they remain an important tool for estimating adverse effects of oil until extensive field work can be done. This study was conducted to measure effects of an oil comparable to that carried by the *Argo Merchant.*

Earlier experiments examined the effects of the water soluble fraction (WSF) of several crude oils on embryonic mortality (Kuhnhold, 1972); however a No. 6 oil consists of a residual distillation fraction of crude oil so it was not possible to extrapolate from crude to a No. 6 oil. Since no samples of the *Argo Merchant* cargo was available to use in the studies, a Venezuelan Bunker C oil (Texas A & M) was used throughout the experiment. Cod was chosen as the test organism since it was available at the Narragansett Laboratory of the National Marine Fisheries Service during the time of the spill and was one of the species spawning in the vicinity of the *Argo Merchant* during monitoring cruises conducted by the Northeast Fisheries Center.

Oil concentrations were chosen that were expected to produce sublethal damage which could lower hatching rates. Heart development and heart beat rates were used as indicators of the physiological status of the test organisms.

Materials and Methods

The cod eggs used in the experiment were spawned and naturally fertilized at 5°-6°C in a tank at the Narragansett Laboratorv of the Northeast Fisheries Center.

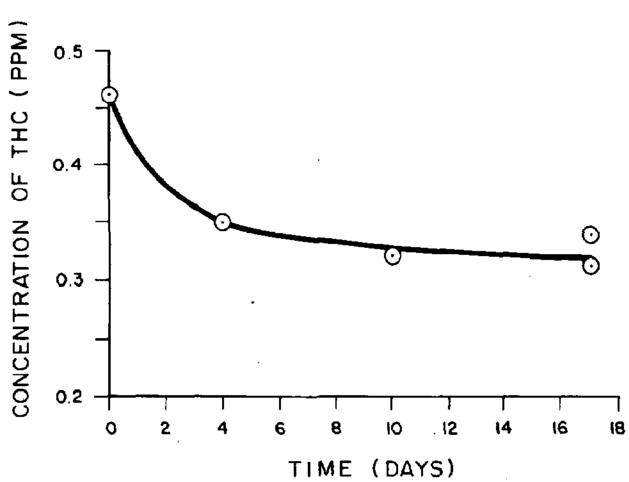

Figure 1. *Curve of hydrocarbon loss of initial (nominal) concentration of 500 ppb total CCl_4-extractable hydrocarbons (THC) of the water soluble fraction of Venezuelan fuel oil No. 6. All concentrations were obtained by dilution of original WSF of 0.72 ppm.*

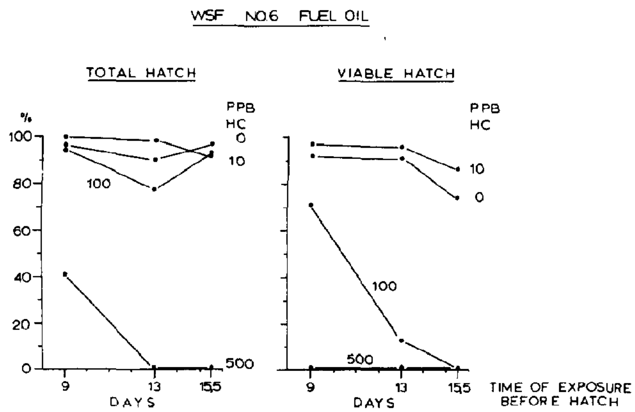

Figure 2. *Comparison of total and viable hatch of cod larvae exposed to the water soluble fraction of Venezuelan fuel oil No. 6 at the given concentrations of total hydrocarbons (THC).*

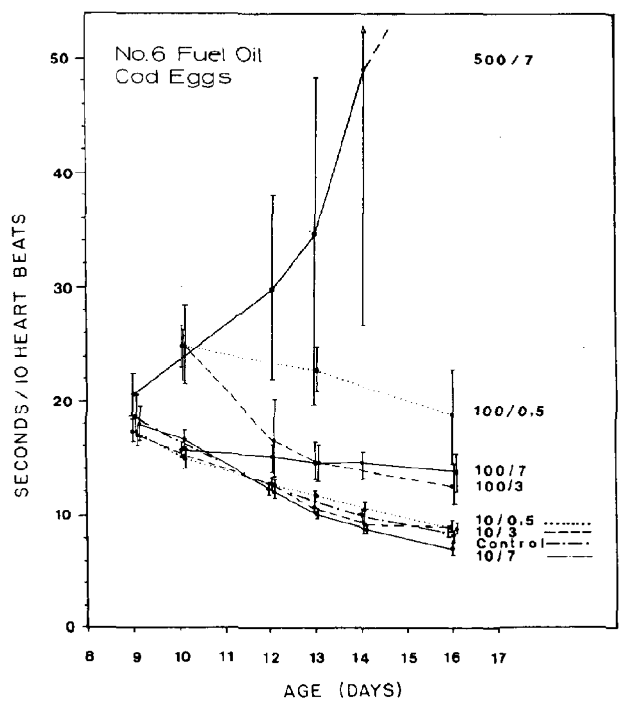

Figure 3. *Influence of the water soluble fraction (WSF) of Venezuelan No. 6 fuel oil on the heartbeat of cod embryos. Exposure ages are 0.5, 3.0, and 7.0 days. WSF concentrations: 10, 100 and 500 ppb. Vertical bars represent standard deviation of 10 measurements.*

One-half, 3, and 7 day old eggs were exposed to an extract of the oil for exposure times of 15.5, 13, and 9 days, respectively. The tests were static (i.e., there was no replacement of the test medium throughout the experiments).

The extraction of the No. 6 fuel oil was prepared according to Hyland (1973) to provide concentrations of water soluble fractions (WSF) comparable to earlier studies. Thirty milliliters of No. 6 fuel oil were slowly

Table 1. LC_{50}'s (initial concentration) ppb of total hydrocarbons of the Water Soluble Fraction (WSF) of Venezuelan fuel oil No. 6 for cod embryos at 3 different ages.

Age of Eggs at Exposure (days)	*For Total Hatch*	*For Viable Hatch*
0.5	150-200	20-30
3	200-250	30-40
7	325-375	150-200

added to the surface of 11.5 liters of filtered seawater in a 15 liter carboy. The water was stirred slowly with a magnetic stirrer for 12 hours without dispersing oil droplets into the water.

The extract was kept under the oil film for another 12 hours before the water phase containing the water soluble fraction was drawn from the carboy. During the test the dissolved compounds were subject to evaporation. Two 1-liter water samples were taken to determine the initial total hydrocarbon concentration using CCl_4-extraction and IR absorption. Standards were made from dilutions of the oil in CCl_4. The loss of total hydrocarbons (THC) from the water was approximately 25% in 4 days, and 32% in 10 days, which can be considered a low reduction in THC (Figure 1). Since no data were available about the actual concentrations of the WSF of the *Argo Merchant* oil at the spill site, initial concentrations of 10, 100, and 500 ppb of total CCl_4-extractable hydrocarbons were used.

Tests were carried out in open 1-liter jars, each containing 100 eggs or larvae and .75 liter of extract. The temperature was 7°C. After hatching, the larvae were held and observed in the jars for 4-5 days. Larvae which survived to this point were considered "viable". At this time most of the yolk is resorbed and the larvae initiate feeding. However, they were not fed in this experiment, as no food source was available. To investigate effects of oil on cod larvae after hatching, 2, 4, and 8 day old larvae from control tanks were transferred to the test jars. These ages were chosen to include the range of first feeding larvae. For cod, the initiation of feeding occurs 5 to 6 days after hatching. If the first feeding does not occur by day 10, the cod larvae do not survive. Exposure of 8 day old larvae would show the effect of delayed feeding in addition to the oil effects.

In order to record heartbeat rates, a random sample of ten eggs was carefully transferred to a glass dish and retransferred to the jar after inspection under a dissecting microscope. The time that elapsed between 10 heartbeats was measured with a stopwatch. Precautions were taken to avoid temperature increase during heartbeat counts.

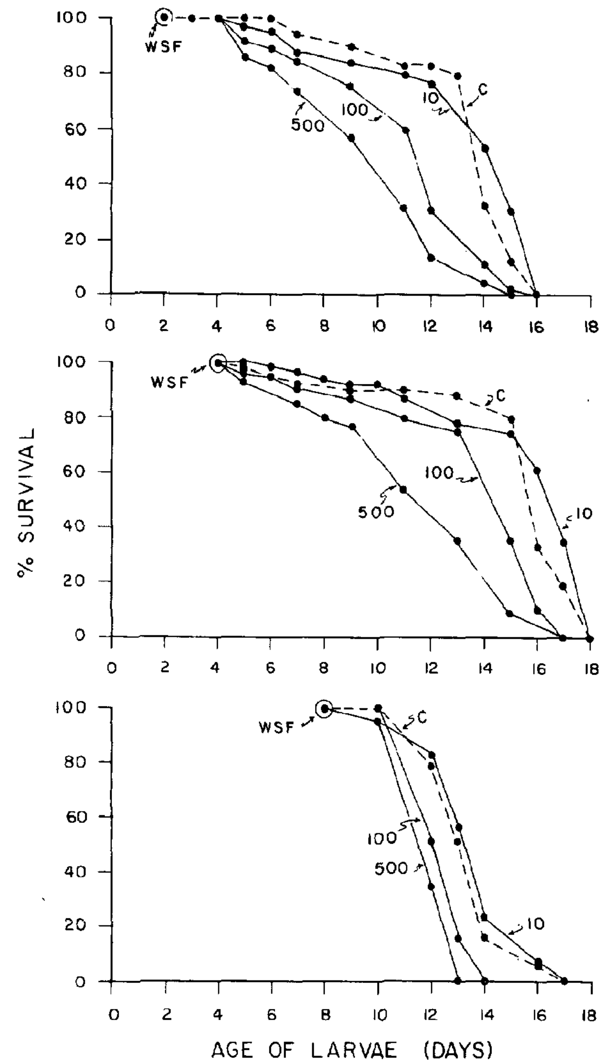

Figure 4. *Survival of unfed young cod larvae exposed to the water soluble fraction (WSF) of Venezuelan No. 6 fuel oil 2, 4, and 8 days after hatching (Temp. 7.0°C).*

Results

Hatching. Ninety-one to 97% of the control larvae were viable, so 3-9% can be considered within the natural range of variability for larval mortality (Figure 2) in this experiment. Of the eggs in the 10 ppb treatment, a maximum of 7% were non-viable, which is within the range of variation of the controls.

However, in the 10 ppb treatment, there was a sharp decrease in viability. In the 0.5 day eggs the "total hatch" rate was normal, but none of the larvae survived more than a few days after hatching. The 3 and 7 day old eggs showed generally no lethal effect until hatching. It is evident that increasing viability is correlated with decreasing exposure time. The ratio of per cent "total hatch" to per cent "viable larvae" for 3 and 7 day old eggs was 78%/13% and 93%/70%, respectively.

The 500 ppb treatment proved lethal for the 0.5 and 3 day eggs. Forty per cent of the 7 day eggs hatched, but none were viable. Table 1 gives the LC_{50} values for "total hatch" and "viable hatch" of 0.5, 3 and 7 day old eggs. These data are interpolated graphically and show the difference between "survival until hatching" and "viable hatch".

Embryo Heartbeat Rates. During normal development (at 7°C) the embryo heartbeat rate was regular by day 9 at an average rate of 19.3 seconds/10 beats (= 31.1 bts/min). At hatching, the rate had increased to 9.1 sec/10 beats (= 65.9 bts/min).

There was no detectable effect on heartbeat rate at 10 ppb total hydrocarbons (Figure 3). One hundred parts per billion had a retarding effect on the development of the heart. The eggs exposed at 0.5 and 3 days did not show a regular heartbeat until day 10 and the rate of 25.5 sec/10 beats (= 23.5 bts/min) was considerably slower than the rates for the control embryos. Although the rates increased with time, they failed to reach the normal rate. It is evident that the rate of increase of heartbeat during development is correlated with the length of time the embryos were exposed to the oil. The 7 day embryos showed no immediate effects, as the heartbeat rate was still within the normal range after three days. However, the heartbeat range did not increase and never exceeded the range for the 3 day eggs.

At 500 ppb, effects could be measured for the 7 day eggs only because mortality was 100% for the 0.5 and 3 day eggs. After 2 days' exposure at day 9 the heartbeat had decreased (20.3 sec/10 beats = 29.6 bts/min) slightly compared to the heartbeat rate of the controls (19.3 sec/10 beats = 31.1 bts/min). However, after one week, the rate had dropped to 50 sec/10 beats (= 12 bts/min) and the beats were extremely irregular so that timing the sequence of beats became difficult. This is shown in Figure 3 by the large standard deviation about the mean beat rate.

It was also observed that as the exposure time increased, more of the eggs slowly lost buoyancy and sank to the bottom of the test jars. In general, the eggs which sank to the bottom had slower heartbeat rates than the remaining floating ones.

Larval Survival. Contrary to previous tests, viable larvae hatched from eggs incubated in clean water were selected for larval survival experiments. At all three ages (2, 4, and 8 days) the survival time of the larvae generally decreased with increasing hydrocarbon concentration (Figure 4). The mean survival times were compared to their corresponding controls only.

Although it appears that the low concentration (10 ppb) actually enhances survival for the 2 and 4 day old larvae, the values at 10 ppb probably reflect the natural variability in survival rates.

The difference in survival times between control and 4 day old larvae is less than for 2 day larvae (Table 2) indicating greater resistance of the 4 day old larvae. The survival time of the 8 day old larvae approached that of the controls with the 50% mortality point occurring only 1-2 days earlier than for the controls.

An additional morphological observation was made on the moribund larvae. At closer inspection a substantial portion of the larvae had an abnormally developed apical part of the primordial fin fold. The fin was swollen and showed, even at relatively low magnification (ca. 50 x), a more irregular surface than in normal larvae (Figure 5). The frequency and degree of this abnormality seemed to be correlated with the oil concentration. In some cases it

Table 2. Effect of the Water Soluble Fraction (WSF) of the Venezuelan fuel oil No. 6 on mean survival time of young unfed cod larvae.

Age at Exposure	*Initial Concentr. of THC (ppb)*	*50% Mortality after (days)*	*Time after Exposure Began (days)*	*Difference in 50% Survival Time between Control and Treated Larvae (days)*
2	0	13.7	11.7	---
	10	14.1	12.0	+0.4
	100	11.6	9.6	- 2.1
	500	9.2	7.2	- 4.5
4	0	15.0	11.0	---
	10	16.3	12.3	+1.3
	100	14.0	10.0	- 1.0
	500	11.4	7.4	- 3.6
8	0	13.4	5.4	---
	10	13.2	5.2	- 0.2
	100	12.0	4.0	- 1.4
	500	11.5	3.5	- 1.9

Table 3. Factors needed for assessment of damage to fish population by spilled oil.

I	*II*
Type of oil spilled	Area of spawning ground
Area covered (contaminated)	Time of spawning
Concentration of dissolved hydrocarbons	Distribution of eggs and larvae (vert. and horiz.)
Chemical characteristics of WSF	Specific sensitivity
Dilution gradient (horiz. and vert.)	Duration of influence

was evident 3 to 4 days after exposure to the WSF, with the larvae still alive but showing signs of reduced viability. However, this phenomenon was not evaluated quantitatively, and histological examinations were not made.

Discussion

Naturally, it is difficult to extrapolate from laboratory findings to the field conditions which existed at the time of the *Argo Merchant* spill. For a comprehensive assessment of the damage to the fish population, several factors must be considered (Table 3). Some of these are known, or at least can be estimated. The largest problem is the lack of adequate data on the concentration of dissolved hydrocarbons in the water at the spill site, the composition of the water soluble fraction, and most important, the change in concentration gradients in the water through time.

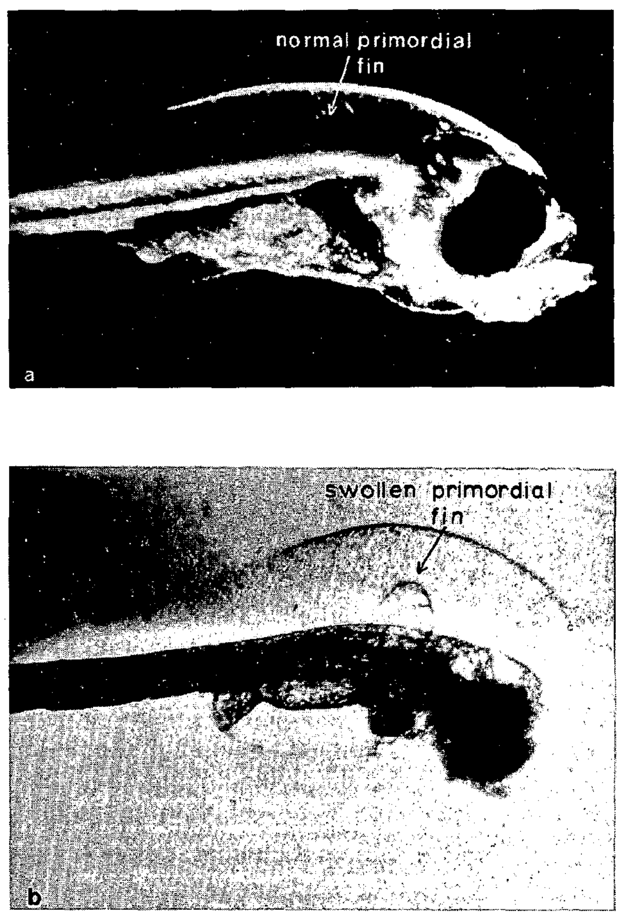

Figure 5. *Deformation of the primordial fin in cod larvae exposed to the water soluble fraction (WSF) of Venezuelan No. 6 fuel oil: a) normal shape of the apical region of the fin, b) deformed swollen fin. The degree of this defect depends on exposure time and WSF concentration but was not evaluated quantitatively.*

UV-analyses of hydrocarbons in water samples taken at various times after the spill and at different locations showed maximum values of 250 ppb THC (NOAA, 1977). The concentrations in the test series were determined by IR spectrometry, so comparison with UV results is difficult.

As all water samples were taken at various times after the spill and at different locations they represent only a few points out of a three dimensional pattern. Assuming that time is the most important factor in this system, and that dilution of the hydrocarbons occurs in horizontal and vertical directions, initial concentrations close to the slicks which were not recorded should have been somewhat higher.

Considering the deleterious effects of oil on cod eggs and larvae measured in the laboratory, it is certainly possible that there were immediate or delayed effects of oil on pelagic fish eggs and larvae in the vicinity of the spill. However, the organisms in the laboratory were continuously exposed to the WSF, whereas the embryos and larvae in the field could have been exposed to varying concentrations of WSF for varying periods of time. Kuhnhold (1972) showed that short term influence on eggs (short in regard to total incubation period: 1 to 4 days) of WSF of crude oils can either immediately manifest deleterious effects or result in gradual effects depending on the type of oil. Physiological measurements had not been made parallel to the hatching counts by Kuhnhold. The measurement of heartbeat rate may be a simple prehatch-parameter to judge viability of larvae; however, short-term effects in larvae (after several hours to 2 days) can be reversible depending on the type of oil to which the larvae are exposed. Different species also vary in sensitivity to the WSF of oils. This means that the time beyond which adverse effects are irreversible in larvae varies from one species to another. This was demonstrated for young larvae of plaice, cod and Norwegian herring, increasing in sensitivity with the order mentioned (Kuhnhold, 1972). These findings suggest the effects of oil on cod in the field should have been generally less severe than under the laboratory conditions.

The extent of damage to the brood population also depends on the horizontal and vertical distribution of eggs and larvae in the spill area. NEFC plankton surveys after the *Argo Merchant* spill showed cod and pollock eggs present (NOAA, 1977). However, the spill did not occur during the peak spawning period of either species and it covered only a minor part of the spawning area (Colton and St. Onge, 1974), so it is difficult to assess the extent of acute damage to the total population.

On the other hand a quite important question arises: What is the secondary effect of the oil on reproduction if it accumulates in the food web and enters adult fish? It has been observed that oil particles are ingested by zooplankters; many individuals of the most abundant species were found with oil in their digestive tracts (Kuhnhold, 1978). As most of the oil seems to pass unaltered through the animals with the feces and is sedimented, it is made available to another section of the food web, which is the food basis for demersal fish species. Recent investigations focused on the effects of incorporated crude oil on the offspring of trout (Hodgins et al., 1977) and of water soluble components of No. 2 fuel oil on offspring of winter flounder (Kuhnhold, 1978). Although the results of these two investigations are contradictory, that is, no visible effects were observed for trout but negative effects on larval survival were observed for winter flounder, one cannot exclude latent effects on offspring in contaminated areas. The question remains: How much does this affect a year class? This question can be addressed with simultaneous laboratory, shipboard, and *in situ* observations. Consideration should be given to the development of new technology to deal with the maintenance and growth of embryos and larvae at sea, following the pioneering work of Lasker (1975) and Laurence (1978).

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Interactions Between Petroleum and Benthic Fauna at the *Argo Merchant* Spill Site

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Abstract

Funding was provided for collection and archiving of quantitative benthic grab samples from the *Argo Merchant* spill site. Oil was found in sediments within 3-4 km of the wreck in February and July 1977. The basis for the conclusions of this report are visual inspection of samples during collection and partial identification of benthos in 14 samples.

The spill occurred on a sand ridge bordered by gravel-bottomed channels. Both sand and gravel environments were exposed to oil. On the ridge continuous movement of sand waves may bury oil, break it into smaller particles, or release it into the water. Sand collected at the bow of the wreck contained 2-0.03 mm diameter oil particles which only weakly adhered to sand grains. Few aggregated or coated grains were seen.

The channel-bottom fauna had a high standing crop of both sessile and motile species in all samples obtained, but could not be described quantitatively. The ridge sand supported few macrobenthos and a relatively homogeneous interstitial community. At the bow of the wreck 4-122 ppm of oil was found in February and 0.2-0.6 ppm in July. There was a slight increase in density and diversity of interstitial benthos at the later date. In the February samples oil was observed in the guts of interstitial harpacticoids and a polychaete *(Ophyrotrocha* sp.) and adhering to the appendages of a burrowing amphipod.

Introduction

I participated in five University of Rhode Island cruises to the area of the *Argo Merchant* grounding. A large number of grab samples were taken for chemical analysis and to archive for possible studies of impact of oil on individual benthic invertebrates and on benthic communities. This report is based on visual inspection of the samples, review of the geology of the spill area, and examination of benthic organisms in a small number of grab samples. These preliminary studies have identified the form of oil in sediments at the spill site, the organisms present at the site, and ways in which these organisms may interact with spilled oil. Additional information on oil analyses and the histopathology of larger organisms obtained on University of Rhode Island cruises is presented by Hoffman and Quinn (1978) and Brown and Cooper (1978).

Methods

Only a few grab samples were obtained on URI cruise EN-002 and EN-003 (December 28-30, 1976; January 26-29, 1977). These included samples from a reference site 30 miles southwest of the spill area and qualitative samples from gravel east of the spill area.

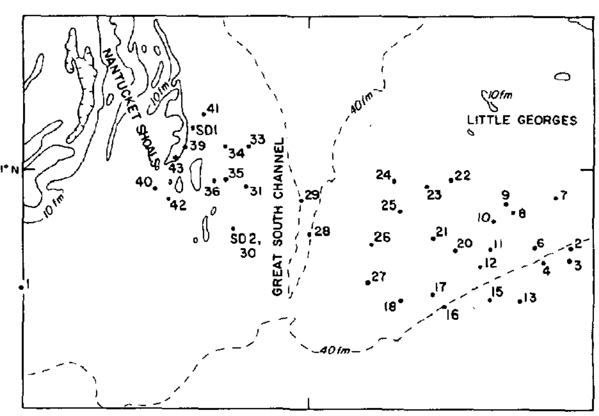

Figure 1. *Station locations, EN-004, February 9-13, 1977. Argo Merchant wreck is adjacent to station 43.*

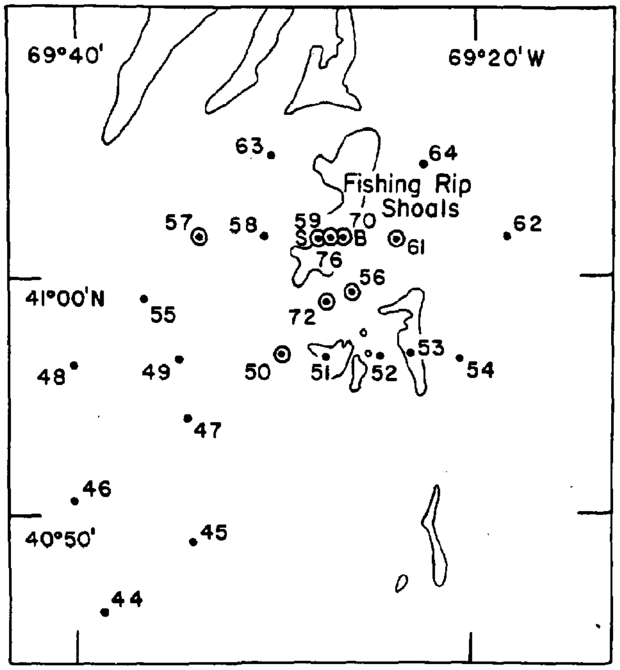

Figure 2. *Station locations, EN-005, February 22-27, 1977. Argo Merchant bow and stern are shown by initials. Stations in which oil was observed are circled. 10 fathom contour shown.*

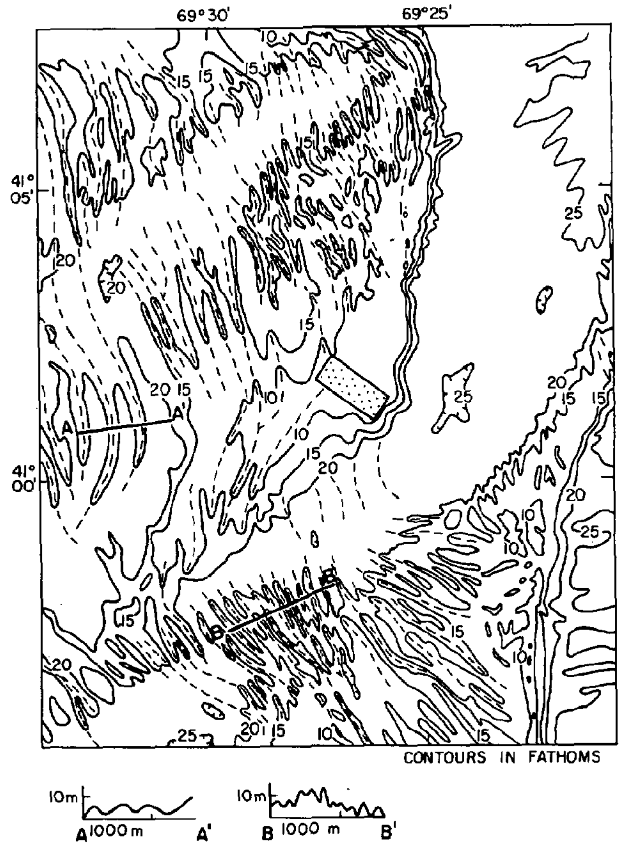

Figure 3. *Topography of Fishing Rip tidal ridge. Location of Argo Merchant wreckage shown by rectangle; dashed lines are the positions of sand wave crests inferred from 1 fathom contours of C&GS map 0708N-53; cross sections AA' and BB' are shown below.*

On EN-004 (February 9-13, 1977) 40 stations were sampled from areas which had been in the path of the floating oil (Figure 1). This area extended 65 miles east-southeast of Fishing Rip, the site of the spill. Oil was found in sediments only in the immediate vicinity of the wreck (Hoffman and Quinn, 1978).

Sampling on EN-005 (February 22-27) was designed to describe the distribution and form of oil in sediments and its impact on organisms in the immediate vicinity of the wreck (Figure 2).

On July 22-24, 1977 a 65' vessel was used to resample oil impacted areas to establish the time course of dispersion and weathering of oil and the long term impact on organisms.

Three 0.1m^2 Smith-McIntyre grab samples were taken at most stations. With the grab weighted to 135 kg full samples were always obtained in coarse sands; however penetration was poor in fine compact sand and sample retention was poor in gravel. Large and small scallop dredges were used to qualitatively sample rocky areas.

Grab samples were divided with a sheet metal plate with half allocated for biological analysis. From this a subsample (35.2 cm^2 x 10 cm) was removed with a length of core tube and preserved separately. Both biological samples were preserved in 10% buffered seawater-formalin with rosebengal dye added on the last two cruises.

I normally separate macrobenthos with a 0.75 mm mesh seive. This was not practical for these samples since many had mean grain sizes of 0.6-1.55 mm. The following flotation technique was developed to separate larger microfauna and macrofauna from the small sub-sample. Preservative and stain is washed out of the sample on a 0.074 mm seive. The sample is slowly added to a 500 ml graduated cylinder containing a dense colloidal silica solution (Ludox; sp. wt. 1.39). A film of tap water is floated on the Ludox (de Jonge and Bouwman, 1977). After one hour animals and particles are pipetted from the Ludox-water interface. This material is washed and preserved. Particles still in suspension in the Ludox are removed on 0.039 mm netting. The sediment is washed and examined under a binocular microscope for heavy bodied animals and for animals or oil particles adhering to sand grains.

After the sediment had been examined an aliquot was removed, dried, seived at 1/2 ϕ intervals, and grain size fractions weighed and retained.

At this time 14 samples have been at least partially sorted. Identification to species will not be possible in soft-bodied meiofauna because of the type of preservation.

Results and Discussion

Geology. The topography of the wreck site is shown in Figure 3. This map suggests how complex and dynamic the area is. Fishing Rip is near the outer edge of a system of sand ridges extending to Nantucket Island. These ridges consist of debris from a former peninsula. Swift (1975) has described the form and possible dynamics of

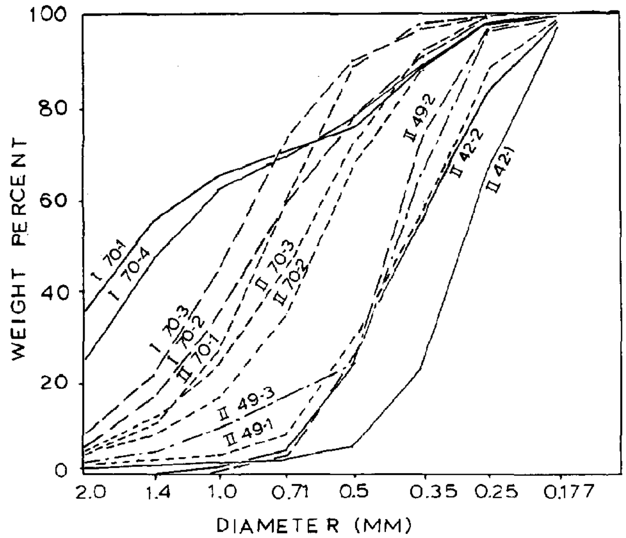

Figure 4. *Cumulative grain size distribution of sediment samples (I and II indicate February and July samples respectively).*

sand ridges in various shelf locations. Figure 3 is drawn in a style similar to Swift's map of the inner Nantucket Shoals.

Major features of this system are northeast-southwest sand ridges parallel to the dominant tidal current flow which are separated by gravel bottom channels. The tendency for the channels to break into ebb and flood sinus couplets is seen south of the wreck site.

Large sand waves, shown by dashed lines, lie parallel to the dominant flow on the ridge flanks. Swift (1975) notes that they become parallel to ridge crests as they get shallower. Sand waves near Fishing Rip are up to 6 meters high and have wavelengths of 150 and 400 meters along the lines shown in the figure. The relatively flat top of Fishing Rip is presumably formed by wind wave dispersion. Smaller sand waves and ripples from tidal currents and surface waves are probably found throughout the sandy area.

The sand on the Nantucket Shoals ridges must be almost always in motion as bed load and in near-bed suspension. Smith (1969) has described rapid erosion and rebuilding of sand waves on a ridge in Vineyard Sound. Waves up to 6 meters high were significantly modified in a half tidal cycle. Smith found that the ridge he was studying was in dynamic equilibrium over long periods. Swift (1975) discussed various mechanisms which could remove sand from channels and deposit it on ridges and conserve the ridge form during marine transgression.

The special nature of this ridge and channel system has a number of consequences on the variables of concern in this study. Once oil reached the ridge surface by vertical transport of small particles or by leakage from sunken portions of the vessel, it was probably buried and mixed with sand to a depth of 2-6 meters. If the oil adhered to sediments there would be a tendency for it to remain on the ridge and not be swept into channels or be carried great distances. If the oil did not adhere to sand and remained buoyant, it could be released by sediment motion and transported away by currents.

The extreme mobility of the sands on Fishing Rip excludes most macrobenthic animals with the exception of the powerful burrowing amphipods. A single surf clam recovered on the ridge appeared to have been swept along the sediment surface. On the other hand, the porous and well oxygenated sand can probably support interstitial meiofauna to a great depth. The stable gravel and rock bottoms of the channels can support dense populations of attached, clinging, and cryptic species.

Within the range of grain sizes present, sorting is probably taking place continuously and varies with the position of samples on sand waves. This is suggested by the unimodal and bimodal grain size distributions found at station I-70 (Figure 4). This variation is important in sediment porosity, permeability, and surface area, and in animal distributions. It is unfortunate that a recording fathometer was not available on any URI cruises so that grain size and oil concentration could be correlated with position of samples on sand waves.

Oil in Sediments. The form of oil in sediments will determine whether it is released during sand movement or is available for ingestion by benthic organisms.

Many oil droplets did not adhere to sand grains, but floated free during sampling, storage washing, and animal flotation. The upper size limit of most of the floating droplets was 1-2 mm. Droplets of 0.1-1.0 mm reached the Ludox surface during animal flotation while droplets of 0.03-0.6mm had a much slower upward velocity and were filtered from the Ludox column.

Microscopic examination of sediments showed that there was little tendency of oil to coat either mineral grains or fragments of shell or echinoderm skeleton. In a 200 cc sample of heavily contaminated sand (I-70-4) only 118 quartz grains and one shell fragment had visible oil on them. Oil totally coated two particles made up of fine sediment, rust, and weathered oil which probably originated on a vessel. There were six aggregates in which 2-3 sand grains were stuck together to form 1 mm particles.

Rings of loosely adhering droplets (0.1 mm) were observed on several sand grains. This pattern resulted when attempts were made to spread oil on wet sand grains and large droplets broke into smaller ones. The continuous movement of sand on Fishing Rip would have a similar tendency to break the oil into smaller and smaller droplets while releasing them into the water column.

The use of dry sediments or sediments coated with wetting agents to sink spilled oil and the observation of oil coated sediments on the upper levels of beaches may give the impression that heavy oils will adhere to wet sand. The fact that they do not may explain why beaches "clean themselves" so well.

The presence of loose droplets of oil rather than coatings on sand grains would make it available to larger selective deposit feeders but less available to very small forms and to those feeding on sand grain coatings.

Oil-Fauna Interaction. The term "interaction" is used because at the present time there is little evidence of "impact" in the form of dead or dying animals or of changes in population densities. Physiological and histological abnormalities have been found in some larger animals, but it is difficult to project these effects in space or time. Three sediment types with characteristic benthic fauna were sampled during this program. The following

Table 1. Number of organisms for selected taxa recovered from sediment at the bow of the *Argo Merchant.* (Core sample 35 cm^2 x 10 cm, seive size 0.074 mm. See Hoffman and Quinn, 1978, for details of hydrocarbon analysis.)

	February 22-27, 1977				*July 22-24, 1976*		
	70-1	*70-2*	*70-3*	*70-4*	*70-1*	*70-2*	*70-3*
Crustaceans							
Harpacticoid copepods	35	24	60	62	109	600	78
Ostracods	6	1	2	–	4	53	20
Polychaetes							
Ophryotrocha sp.	–	22	3	4	1	5	2
Polychaete A	1	11	–	–	–	2	2
Nemetodes	7	7	10	10	8	72	80
Soft bodied forms (turbellarians and small nemerteans)	30	45	25	19	28	51	50
Minimum number of species	9	8	6	4	11	12	13
Total individuals	88	111	107	95	156	794	248
Mean grain diameter (mm)	1.55	0.80	0.93	1.3	0.74	0.60	0.66
Hydrocarbons (μg/gm dry wt.)	11.5-19.7	–	4.0-10.2, 34.7	5.1-122	0.4-0.6	0.2	<0.2

sections describe them and interactions with spilled oil which were observed or hypothesized.

1) At reference station 1 (44 m) and at the deep eastern stations (80-90 m), fine compact sand is found with abundant macrobenthic species. Free burrowing amphipods and isopods are numerically dominant. Sand dollars are found in shallower areas and ocean quahogs in deeper areas. Oil was never found in sediments of this type and so samples from these areas will be archived.

2) Gravelly sediments in Great South Channel and in the channels between sand ridges near the wreck site support diverse faunal assemblages. Biomass may be very high, particularly where the horse mussel *(Modiolus modiolus)* is present. A 0.1 m^2 sample in loose gravel from station 2-2 contained over 37 species and 598 individuals. A 1000 cc mass of sponge and colonial tunicate from dredge station 64 contained over 27 macrobenthic species and 224 individuals. Although sessile suspension feeders make up the greatest biomass in these areas, species of all purchase and feeding types are found. A large polychaete *(Nereis pelagica)* and a bivalve *(Hiatella arctica)* occupy burrows in sponge. Brittle stars, scale worms, nudibranchs, and turbellarians crawl on surfaces. Deposit feeding polychaetes are present, possibly taking advantage of biodeposits of horse mussels. Crabs and starfish are present but not usually sampled by grabs. These areas are important in providing food for ground fish (Wigley, 1968).

Gravel bottom fauna was exposed to oil in the channel east of the wreck site. Hoffman and Quinn (1978) found relatively high concentrations at Station 56 and trace amounts at Stations 61 and 50, north and south of Station 56. The presence of small particles of oil in surrounding sands and the observations of Forrester (1971) on the production of large numbers of oil particles following the *Arrow* spill suggest that at times the gravel bottom fauna was exposed to high concentrations of suspended oil.

Brown and Cooper (1978) report on the pathology of a hermit crab from the channel bottom adjacent to the *Argo Merchant* bow. This individual had apparently been exposed to a large mass of oil which it had consumed. Some horse mussels examined may also have been affected by oil. Thurberg and Gould (1978) observed depressed gill tissue oxygen consumption in sea scallops and horse mussels from the spill site soon after the spill. This may be a result of filteration of suspended oil particles.

I know of no analysis in which oil was found in the gills, guts, or pseudofeces of suspension feeders. It would be necessary to take samples for such analyses before oil was cleared from the digestive system.

In summary, the channel areas around the Fishing Rip ridge are difficult to sample quantitatively; they are physically heterogeneous and probably received doses of particulate oil and water soluble fractions which were variable in concentration and duration. Examination of individual animals is the only way to detect impact on the hard bottom. A knowledge of the community makeup and the life history of the fauna can be used to guide choice of species for analysis.

3) The final sediment type sampled was the motile, shelly sand making up Fishing Rip ridge and areas to the southwest. It would be inaccurate to call the macrobenthos of this area a "community" since the term suggests biological interaction and constancy. This fauna could be considered a remnant of a community in a less active bottom.

The populations of interstitial meiofauna appear to

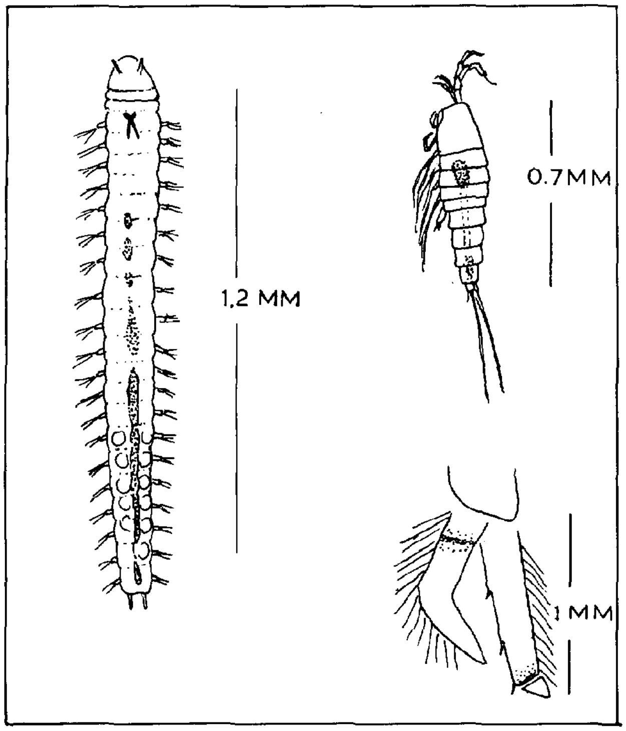

Figure 5. *Examples of interactions between benthic organisms and oil from February samples. A polychaete (Ophryotrocha sp.) and a harpacticoid copepod contain ingested oil (sta. 70-2). Oil adheres to an appendage of the amphipod Psammanyx nobilis (Sta. 50-1); there is no tissue distal to the oil.*

be more consistent. At this time I have no counts from a coarse sand reference station. Counts from an impacted station in February and July (Table I) show that harpacticoid copepods and turbellarians are numerically dominant while nematodes are relatively unimportant. It is difficult to compare these counts with published densities because a large seive size was used (0.071 vs. the usual 0.044 mm). Furthermore, only the surface 10 cm was sampled and it is not known to what depth the fauna penetrate. Penetration to one meter would give densities per m^2 comparable to those found in a sandy beach by McIntyre and Murison (1973): harpacticoids 70,000-1,700,000 vs. 1,000,000 and total meiofauna 250,000-2,300,000 vs. 500,000-6,700,000.

Interstitial species could interact with oil within sediments by contact or ingestion of droplets or by exposure to toxic soluble fractions released in interstitial water. Ingestion is possible because most of the individuals are deposit feeders.

Examples of interaction of animals with oil are shown in Figure 5. Oil was found adhering to the uropod of a large burrowing amphipod. Tissue appears to have disappeared distal to the rings of oil. Other investigators have found oil adhering to mouthparts and posterior appendages of amphipods (Sanders, 1978).

In two heavily contaminated samples half the *Ophryotrocha* sp. and a few percent of the larger harpacticoids had ingested oil. *Ophryotrocha* is of particular interest because members of this genus have been cultured as bioassay organisms by Akesson (1975). The species studied had generation times of about one month and are deposit feeders resistant to many stresses. While the species found on Nantucket Shoals may not be resistant to pollutant stresses, the fact that it feeds on oil does suggest an opportunistic life style. The counts of *Ophryotrocha* sp. made so far show no change between February and July.

Oil ingestion by calanoid copepods has been observed at oil spill sites by Conover (1971) and Maurer (1977). Spooner and Corkett (1974) found that feeding slowed in calanoid copepods in a suspension of equal numbers of oil and phytoplankton particles and a concentration of 10 ppm of oil. It was thus not surprising to find harpacticoid copecods also ingesting oil. Harpacticoids as a group may be considered stress resistant. Some species are known to have high tolerance to oil (Dalla Venezia and Fossato, 1977). It is not known whether the slight increase in harpacticoid numbers found at Station 70 represents natural variation, recovery after decrease caused by oil, or even failure to reach a higher natural density because of the oil.

I do not have enough data to make conclusions about variation in population numbers or diversity, or about secondary effects. Sanders (1978) examined three grabs from two stations 10 km west of the wreck in December 1976, when no oil was present, and again in February 1977, when oil was visible in the sediments. He found a consistent decline in densities of many small polychaetes including the dominant syllid species which he interprets as due to transported particulate oil.

Drastic reduction in all meiofaunal groups took place over five months in enclosed marine ecosystems in which light fuel oil was held at around 150 ppb (Elmgren, 1978). Such a non-specific response might not be the case where oil ingestion is significant. Percy (1976) contrasts a scavenging amphipod which would not eat oil tainted fish and an isopod which was "oblivious to presence of oils". Percy found that the isopod was also resistant to the toxic effects of oil. If such a relationship was generally true, oil ingestors would not be differentially eliminated.

In conclusion I recommend that analyses be completed on the small number of oil-containing samples taken by various investigators and the data integrated. In addition, more attention should be given to particulate oil within permeable sediments. When oil particles are considered, rather than water accommodated fractions, oil concentration is less important than the fraction of an individual organism's food which is oil. The Nantucket Shoals area directly affected by oil is comparable to ocean beaches in degree of sediment movement and dominance of interstitial fauna. Observations on the size, weathering, release, and ingestion of droplets discussed in this report are important in predicting the fate and effects of oil on beaches which are sites of both chronic and catastrophic grounding.

Acknowledgments

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Fish Predation on Oil-Contaminated Prey from the Region of the *Argo Merchant* Oil Spill

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Abstract

The stomach contents of 21 species of fish and squid were analyzed to determine the potential impact of *Argo Merchant* oil on the fish stocks in the Northwest Atlantic. Important prey groups found in the stomachs of predators sampled in the region of the oil spill included amphipods, polychaete worms, rock crabs, and American sand lance. The quantities and types of foods eaten by each predator were similar to data previously collected. Amphipods covered with oil were found in the stomachs of Atlantic cod and little skate. Although no oil was found in their stomachs, American sand lance were found to feed on the same genera of copepods previously noted to be contaminated with *Argo Merchant* oil. Predator-prey relationships showed that 81 percent of the predators that were represented ate amphipods and 43 percent ate American sand lance, thus establishing two potential pathways for the oil to have been passed on to the higher trophic levels.

Introduction

The oil tanker *Argo Merchant* ran aground on Fishing Rip, 29 nautical miles southeast of Nantucket Island, Massachusetts, on December 15, 1976. At the time, she was carrying 7,700,000 gallons of No. 6 fuel oil, most of which was released into the environment on December 21 when the ship broke in half. This resulted in one of the largest and most extensively studied oil spills in U.S. history (Grose and Mattson, 1977).

Following the *Argo Merchant* shipwreck a number of biological studies were initiated to assess the impact of the oil on the ecosystem. Although winds and currents carried the oil offshore, eliminating the direct threat of oil on the New England coast, there was concern about the effect of oil on the fish stocks. Contamination of the fish, or fish eggs, and their invertebrate prey could have a long-term effect on the Georges Bank fishery.

The purpose of this paper is to summarize the findings of the investigation of the impact of the *Argo Merchant* oil spill on the food habits of demersal marine fish and squid, and to demonstrate the potential pathways for the transfer of oil residues through the food web.

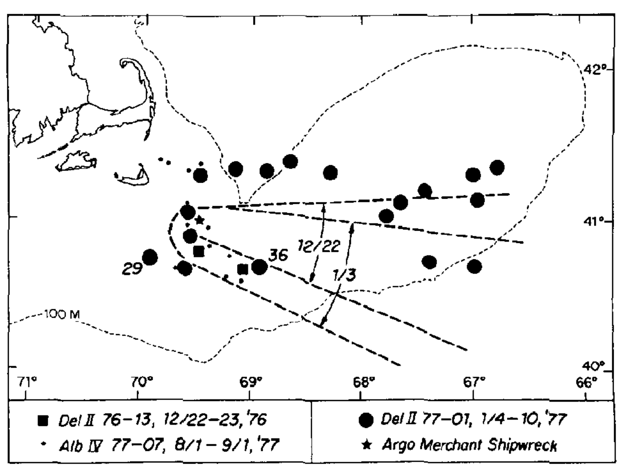

Figure 1. *Location of stations in the vicinity of the Argo Merchant shipwreck where fish and squid were collected for stomach-contents analysis. The three cruises are indicated in the figure. Stations 29 and 36, where oil was found in the stomachs of Atlantic cod and little skate, respectively, are indicated by the appropriate station numbers. Stylized oil-slick borders, shown in the figure as dashed lines, are for December 22, 1976, and January 3, 1977.*

Table 1. Stomach contents of fish and squid collected in the vicinity of the *Argo Merchant* oil spill. The data are expressed as a percent of the total quantity of prey consumed by each predator. The number of stomachs examined, the number found empty, the average weight of prey per stomach, and the length range of the fish examined is given for each predator at the bottom of the table.

	Predator Species								
Stomach-contents group	*Smooth dogfish*	*Spiny dogfish*	*Little skate*	*Winter skate*	*Thorny Skate*	*Alewife*	*Atlantic cod*	*Haddock*	*Silver hake*
Cnidaria		3.3	0.1	0.1		+	+	59.5	
Polychaeta	0.2	0.1	8.7	28.6	29.5		1.7	24.2	
Crustacea	98.9	18.5	73.5	7.0	4.1	99.1	32.4	1.4	97.8
Amphipoda		0.7	43.7	+	+	96.6	11.3	0.8	83.8
Isopoda			1.3	1.3			0.2	0.2	0.3
Cancridae	88.5	15.2	15.4	0.2			9.5		
Other Decapoda	10.4	2.6	12.5	5.5	4.1		9.5	0.4	11.0
Other Crustacea		+	0.6	+		2.5	1.9	+	2.7
Mollusca		31.9	3.5	6.6	0.1		1.3	2.0	
Bivalvia		12.2	0.7	6.6			0.5	1.9	
Gastropoda							0.8	0.1	
Cephalopoda		19.7	2.8		0.1				
Echinodermata							+	1.3	
Echinoidea							+	0.1	
Ophiuroidea								1.2	
Urochordata									
Pisces	0.8	42.3	6.8	43.6	43.4		62.1	1.6	0.1
Rajidae		5.9							
Clupeidae		2.5							
Gadidae		5.9	2.8						
Ammodytidae	0.2	1.4	2.7	36.4			44.4	1.6	
Other pisces	0.6	26.6	1.3	7.2	43.4		17.7		0.1
Miscellaneous	0.1	3.7	6.5	13.9	22.9	0.9	2.2	0.4	2.1
Sand and Rocks		0.2	0.9	0.2			0.3	9.6	
Number examined	8	68	89	23	4	10	81	21	14
Number empty	0	18	7	4	0	0	3	2	6
Mean weight per stomach (g)	91.8	7.0	2.0	6.3	17.3	2.5	18.1	11.3	0.4
Length range (cm)	93-101	30-100	30-51	52-104	73-85	22-49	33-100	34-72	20-38

Materials and Methods

Stomachs were collected from fish and squid caught with an otter trawl during three cruises conducted by the Northeast Fisheries Center (NEFC). The first two cruises were carried out immediately after the spill by the R/V *Delaware II* during December 22-23, 1976 (*Delaware II* 76-13), and January 4-10, 1977 (*Delaware II* 77-01) (Figure 1). A follow-up cruise, 8 months later, was carried out by the R/V *Albatross IV* during August 1-September 1, 1977 (*Albatross IV* 77-07) (Figure 1). A total of 514 stomachs from 21 species of fish and squid was collected during the three cruises. The stomachs were excised aboard ship, individually labeled according to species, length, sex, station, and cruise, and then preserved in 10% formalin. At the NEFC's Woods Hole Laboratory the stomachs were opened and the contents washed onto a fine-mesh screen. The stomach contents were then transferred to trays, manually sorted, identified to the lowest possible taxon, blotted dry, weighed to the nearest 0.001 g, and the weight recorded. Results are presented as the percent that each prey group contributed to the total weight of all stomach contents for each predator. The actual weight constituting each prey group may be calculated by multiplying the mean weight per stomach by both the number of fish examined and the appropriate percent weight. Stomachs were considered empty when the amount of any debris found in the stomach weighed less than 0.001 g. All common names of fish mentioned in the text and tables are those recommended by the American Fisheries Society (Bailey, 1970).

Results and Discussion

Contaminated Prey. Three hundred and five stomachs from 16 species of fish were collected on the first two cruises. Oil, which was subsequently identified as the same type of oil carried by the *Argo Merchant* (see MacLeod et al., 1978), was found on prey in the stomachs of two species of fish. In two Atlantic cod stomachs, gammaridean amphipods (*Gammarus annulatus* and *Anonyx sarsi*) were fouled with oil. These fish were caught at Station 29, which was approximately 25 nautical miles southwest of the wreck.

Table 1. (cont.)

Stomach-contents group	Pollock	Red hake	Ocean pout	American sand lance	Butter-fish	Sea raven	Longhorn sculpin	Window-pane	American plaice
	Predator Species								
Cnidaria		3.9	0.1			+		+	
Polychaeta		5.1	10.1				0.5	1.9	93.5
Crustacea	29.6	76.3	12.6	50.0	1.0	82.5	97.2	74.9	
Amphipoda	0.2	16.3	1.9			+	6.6	54.0	
Isopoda		1.1	0.1				0.2	+	
Cancridae		14.0	9.2			82.5	2.3		
Other Decapoda	7.5	2.8	0.2			+	64.2	20.5	
Other Crustacea	21.9	42.1	1.2	50.0	1.0	+	23.9	0.4	
Mollusca	+	0.6	+			+	0.2		
Bivalvia		0.6	+				0.2		
Gastropoda									
Cephalopoda	+					+			
Echinodermata			70.7						6.5
Echinoidea			70.7						
Ophiuroidea									6.5
Urochordata					99.0				
Pisces	69.8	0.6				9.0	1.1	13.3	
Rajidae									
Clupeidae									
Gadidae						0.1			
Ammodytidae	68.0						0.9	11.4	
Other pisces	1.8	0.6				8.9	0.2	1.9	
Miscellaneous	0.2	2.3	1.5	50.0		0.1	1.0	9.9	
Sand and Rocks	0.4	11.2	5.0			8.4			
Number examined	10	19	17	8	2	9	22	33	5
Number empty	0	1	1	3	0	2	3	17	3
Mean weight per stomach (g)	23.0	0.9	12.4	0.001	0.3	17.3	1.1	0.8	0.4
Length range (cm)	28-87	26-39	46-81	13-19	18	18-32	23-31	27-38	28-48

Oil was also found on a caprellid amphipod in the stomach of one little skate which was collected at Station 36 (Figure 1).

Food Habits. The food habits of fish and squid from the area of the *Argo Merchant* shipwreck have been summarized in Table 1 and differ little from previous published and unpublished data on the food habits of fish from the Northwest Atlantic (Bigelow and Schroeder, 1953; Leim and Scott, 1966; Tyler, 1971, 1972; Bowman, 1975; Maurer and Bowman, 1975; Bowman et al., 1976). However, several noteworthy observations were made during this study. Apparent local abundances of certain prey items have influenced the food habits of two species of fish. First, spiny dogfish were found to have fed on sea scallop (*Placopecten magellanicus*) viscera which constituted 12.2% (see Bivalvia, Table 1) of their diet. Very little shell or adductor muscle was found in their stomachs. Researchers in the past noted that haddock and Atlantic cod also fed on sea scallop viscera (Wigley, 1956; Bowman, 1975). This was due to scallop fishermen cleaning the scallops and discarding the viscera while at sea. Secondly, the most noticeable deviation in diet from previous data was shown by the haddock, which at one station fed heavily on cerianthid anemones. This prey is not usual in the haddock's diet, and yet accounted for 59.5% of the stomach contents weight. Haddock in this region have previously been noted to feed mainly on crustaceans, mollusks, echinoderms, worms, and fish (Wigley, 1956; Wigley and Theroux, 1965; Bowman, 1975).

Major Prey. The analysis of fish and squid stomach contents showed that the majority of the predators from the area of the *Argo Merchant* shipwreck utilized four main prey groups: amphipods, polychaete worms, rock crabs *(Cancer)*, and American sand lance. The importance of these foods was established by determining the number of predators which had eaten the same prey group and the quantity of that prey consumed by each predator. If a given prey group was eaten by more than 40% of the predators and made up 5% or more of the total stomach-contents weight for all of the 21 predators, it was considered major prey.

Calculations made directly from Table 1 show that 60% of the total stomach-contents weight of the 21

Table 1. (cont.)

Stomach-contents group	*Predator Species* Yellowtail flounder	Winter flounder	*Illex illecebrosus*
Cnidaria	+	32.8	
Polychaeta	38.9	5.1	
Crustacea	44.4	54.3	5.1
Amphipoda	29.7	51.3	+
Isopoda	0.3	+	
Cancridae		0.2	
Other Decapoda	14.1	2.7	0.3
Other Crustacea	0.3	0.1	4.8
Mollusca	4.0	0.4	
Bivalvia	3.7	0.3	
Gastropoda	0.3	0.1	
Cephalopoda			
Echinodermata		+	
Echinoidea			
Ophiuroidea		+	
Urochordata		4.4	
Pisces	+	+	66.9
Rajidae			
Clupeidae			
Gadidae			
Ammodytidae			
Other pisces	+	+	66.9
Miscellaneous	7.8	1.5	28.0
Sand and rocks	4.9	1.5	
Number examined	40	19	10
Number empty	10	7	3
Mean weight per stomach (g)	0.9	1.0	0.9
Length range (cm)	23-42	18-46	21-24

predators was composed of the four main prey groups previously mentioned. Each of these groups is discussed below from the standpoint of: (1) the percent each group constituted of the total stomach-contents weight for all predators combined, (2) the number of predators found with each particular prey in their stomachs, and (3) the fish and squid whose diet contained more than 10% by weight of each prey group.

Amphipods, primarily the gammaridean amphipod *Gammarus*, made up 7.9% of the total stomach-contents weight and were found in the stomachs of 17, or 81%, of the 21 predator species. The largest quantities of amphipods occurred in the stomachs of the alewife (96.6%), silver hake (83.8%), windowpane (54.0%), winter flounder (51.3%), little skate (43.7%), yellowtail flounder (29.7%), red hake (16.3%), and Atlantic cod (11.3%).

The second prey group, polychaete worms, constituted 4.9% of the weight of the stomach contents and were eaten by 14, or 67%, of the predators. They were heavily preyed upon by American plaice (93.5%), yellowtail flounder (38.9%), thorny skate (29.5%), winter skate (28.6%), haddock (24.2%), and ocean pout (10.1%).

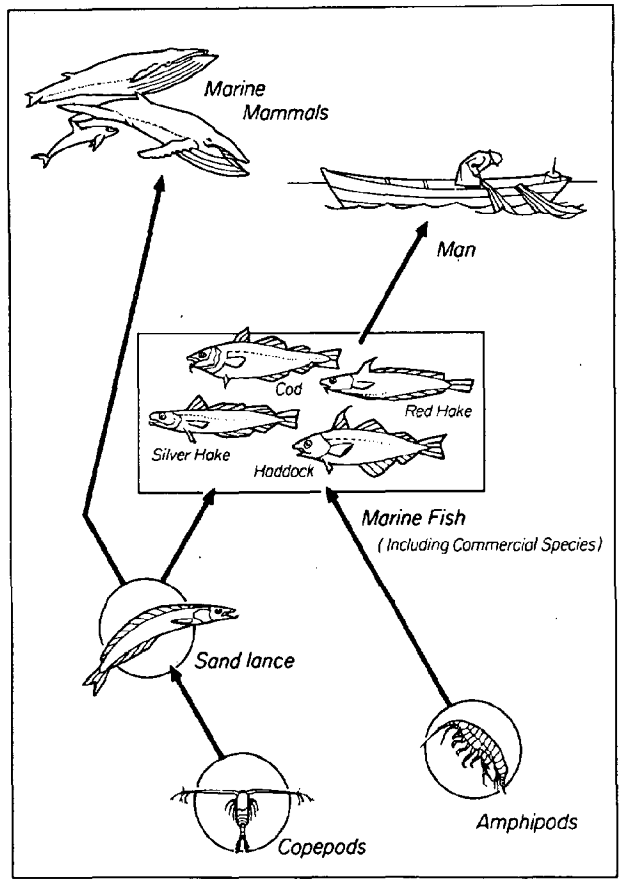

Figure 2. *Two potential pathways for the transfer of oil residues through the food web.*

Rock crabs accounted for 25.6% of the total stomach-contents weight and occurred in 10, or 48%, of the 21 predators. Large quantities of these crabs were found in the stomachs of smooth dogfish (88.5%), sea raven (82.5%), little skate (15.4%), spiny dogfish (15.2%), and red hake (14.0%).

The last major prey, American sand lance, represented 21.6% of the total weight of the combined stomach contents. Nine, or 43%, of the 21 predators utilized sand lance as prey. They were found in large amounts in the stomachs of pollock (68.0%), Atlantic cod (44.4%), winter skate (36.4%), and windowpane (11.4%).

Food Web Transfer of Oil. Reports on the accumulation and transfer of oil through the food web have been published by a number of different authors (see reviews in Wolfe, 1977; Malins, 1977). Zooplankters, for example, have been observed to ingest oil droplets suspended in the water column following several oil spills (Conover, 1971; Maurer, 1977). In the laboratory it has been shown that zooplankton, in particular *Calanus helgolandicus*, will accumulate hydrocarbons from their diet and that this is a more important route for the biological transfer of petroleum residues than uptake directly from solution (Corner et al., 1976). Brown shrimp *(Crangon crangon)* were also reported to eat sunken crude oil during laboratory studies on the toxicity of oil that had been deposited on the bottom, after treatment with a sand-slurry and wetting agent (Blackman, 1972). In a later study, Blackman (1974) found that oil-contaminated shrimp were eaten by plaice *(Pleuronectes platessa)* more frequently than the uncontaminated controls. He concluded that the oil affected the shrimps' behavior and made them more available for predation. In the same study it was found that plaice would intentionally eat sunken crude oil. Horn et al. (1970) showed that prey associated with tar balls in the Mediterranean Sea and eastern North Atlantic Ocean were readily consumed by the saury, an epipelagic fish and important component of the ocean food web.

Following the *Argo Merchant* shipwreck, oil was not found in large quantities or as isolated clumps in the fish stomachs examined. It is clear, however, that prey contaminated by oil was not avoided. The significance of this observation is that it establishes several pathways by which oil could be transferred to higher trophic levels (Figure 2). The identification of oil in the gut of several species of copepods (Maurer, 1977) forms the basis of one of two pathways. Three genera of these copepods, *Calanus, Centropages,* and *Pseudocalanus,* were identified as prey of the American sand lance. The sand lance itself is a very important prey of many commercial fish species, i.e., Atlantic cod, haddock, and yellowtail flounder (Scott, 1968). The sand lance is also a potential prey of whales (Bigelow and Schroeder, 1953; Nemoto, 1959; Overholtz and Nicolas, 1978), thus extending the pathway for the transfer of oil residues to higher marine trophic levels.

The second pathway begins with amphipods, such as those that were contaminated with oil, which are an extremely important prey of marine fish. Over 40 different species of fish in the Northwest Atlantic are known to prey on amphipods (Maurer and Bowman, 1975). Furthermore, juvenile fish of such species as Atlantic cod, haddock, silver hake, red hake, yellowtail flounder, American plaice, and winter flounder depend heavily upon amphipods as a food source (Bigelow and Schroeder, 1953; Leim and Scott, 1966; unpublished observations). Since many of these species are exploited commercially, this extends the pathway of oil directly to man.

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Effect of the *Argo Merchant* Oil Spill on Bird Populations off the New England Coast, 15 December 1976 – January 1977

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Abstract

Bird observations were conducted near the site of *Argo Merchant* from 15 to 24 December 1976. During that period 1120 birds of 13 species were recorded. Almost 92 percent of the birds sighted were gulls; Great Black-backed *(Larus marinus)*, Herring *(L. argentatus)*, and Black-legged Kittiwake *(Rissa tridactyla)*. Approximately 59 and 41 percent of the total number of Herring and Great Black-backed Gulls, respectively, were visibly oiled. Observations made at sea during January 1977 indicated that more birds were present outside the oil slick area but a larger proportion of visibly oiled birds were within the affected area.

From 20 December 1976 to 24 January 1977, 69 live and 112 dead birds of 16 species were collected from the beaches of Nantucket Island and Martha's Vineyard. Alcids (49%), gulls (27%), and loons (19%) were the most numerous species found. Fifteen specimens of 5 species of beached birds were examined internally, and it was found that the lungs and kidneys were the vital organs most seriously affected.

Although bird abundances are difficult to estimate at sea, and shore counts of beached birds are not representative or accurate of actual mortality from an oil spill, data indicate that the *Argo Merchant* spill probably had minimal effects on coastal and marine bird populations off the New England coast.

Introduction

Oil spills and oil pollution present hazards to coastal and marine birds. Previous authors have based their estimates of total mortality from coastal and offshore spills by determining the species and numbers of oiled birds found on beaches (Bourne et al., 1967; Greenwood et al., 1971; Hope-Jones et al., 1970; Brown et al., 1973). Shore counts of live and dead oiled birds, however, give a distorted and inadequate picture of the actual mortality suffered from a spill (Taning, 1952; Hawkes, 1961; Erickson, 1962; Hope-Jones et al., 1970). Therefore, this study presents information gathered at sea on the distribution of oiled and non-oiled birds during and after the *Argo Merchant* spill.

Although the physiological effects and toxicity of oil on waterfowl have been examined (Hartung, 1963, 1964, 1965, 1967; Hartung and Hunt, 1966), no comparable information has been documented for marine birds. In this study, necropsies were performed on a sample of birds killed by the *Argo Merchant* spill to determine which organs were affected, and the probable causes of death.

Methods

Pelagic Observations. From 15 to 24 December 1976, bird observations were made during daylight hours from the USCGC *Vigilant*, which was positioned near the grounded tanker, *Argo Merchant*. Species, abundance, and behavior of each bird sighting were recorded as well as the occurrence of oiled plumage.

In January, 1977, quantitative bird observations were made during three cruises to Nantucket Shoals and Georges Bank. The cruises were on R/V *Delaware II* from 4-10 January, USCGC *Decisive* from 21 January to 02 February, and R/V *Endeavor* from 26-30 January. Observations of common to abundant species were quantified using "acceptable 10-minute watches." An acceptable 10-minute watch is a count of the total number of each

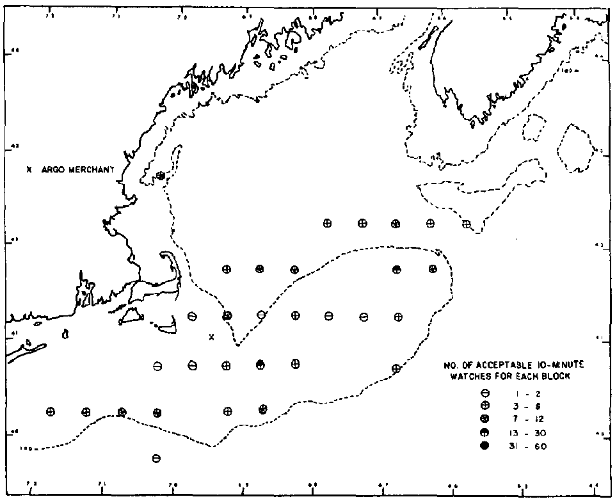

Figure 1. *Effort, January 1977.*

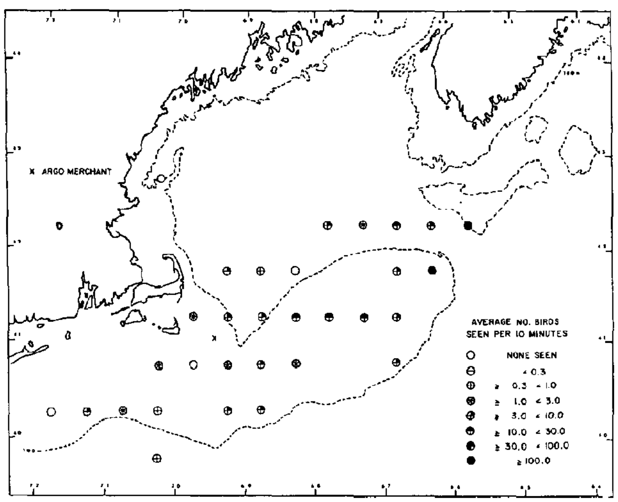

Figure 2a. *Distribution of Northern Fulmar, January 1977.*

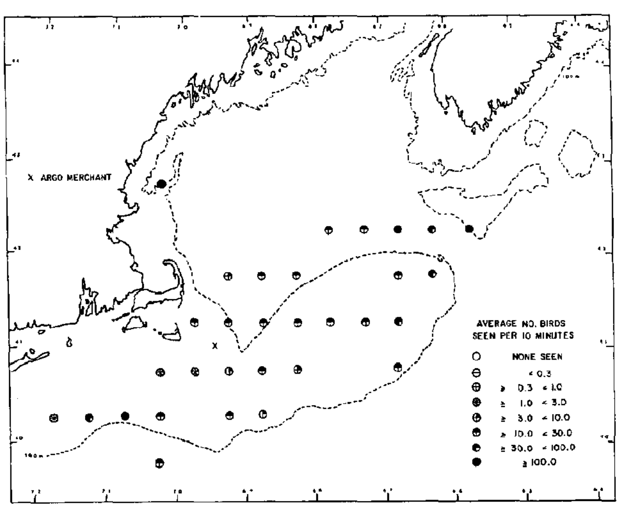

Figure 2b. *Distribution of Great Black-backed Gull, January 1977.*

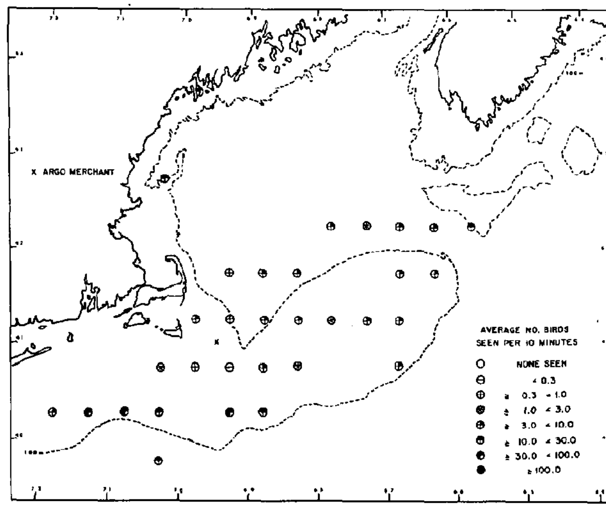

Figure 2c. *Distribution of Herring Gull, January 1977.*

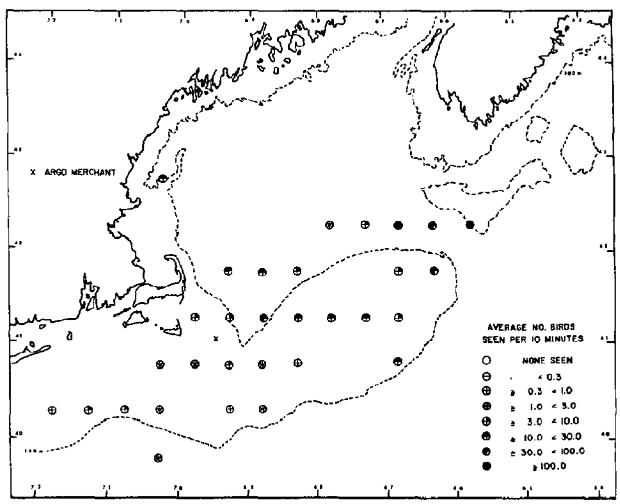

Figure 2d. *Distribution of Black-legged Kittiwake, January 1977.*

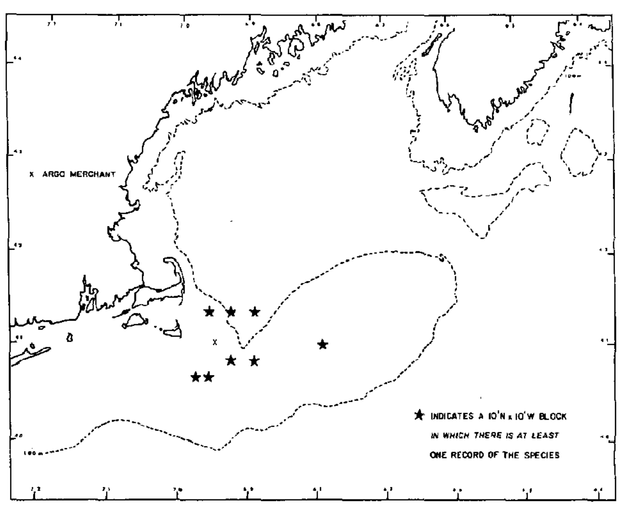

Figure 3a. *Sightings of Large Auks, January 1977.*

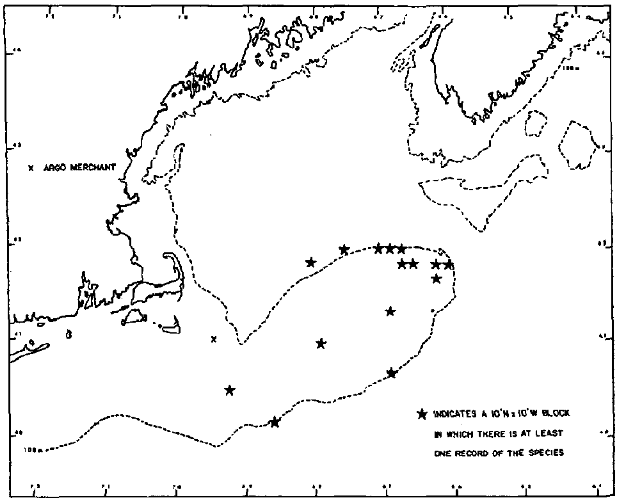

Figure 3b. *Sightings of Dovekies, January 1977.*

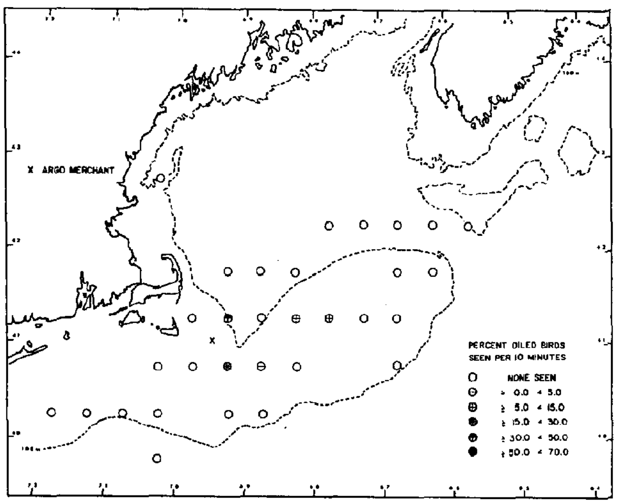

Figure 4a. *Distribution of Oiled Northern Fulmars, January 1977.*

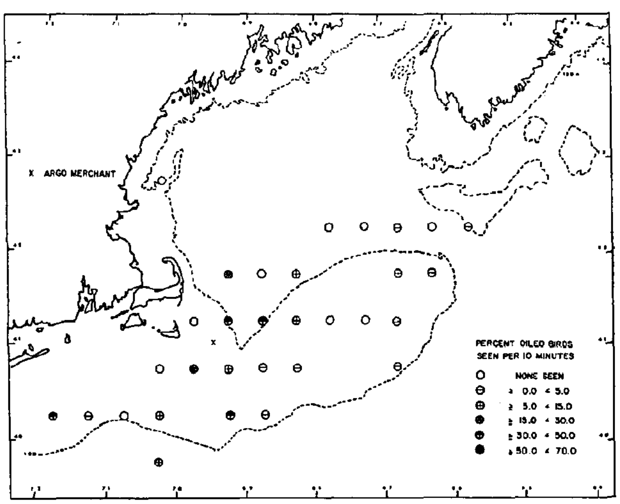

Figure 4b. *Distribution of Oiled Great Black-backed Gulls, January 1977.*

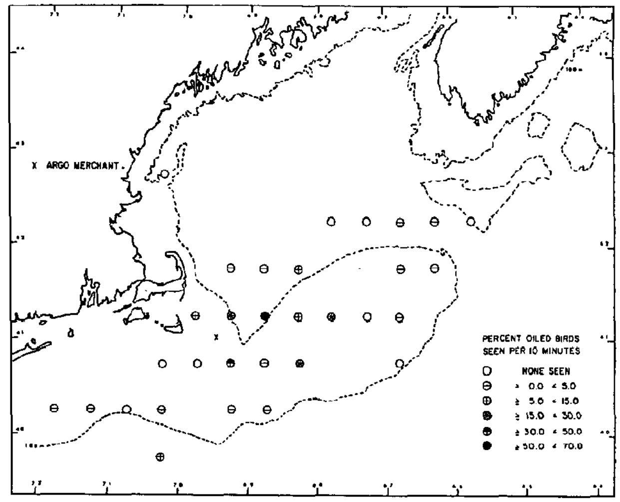

Figure 4c. *Distribution of Oiled Herring Gulls, January 1977.*

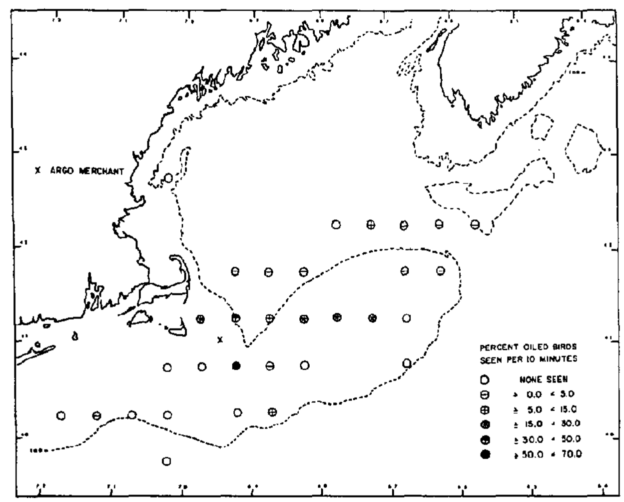

Figure 4d. *Distribution of Oiled Black-legged Kittiwakes, January 1977.*

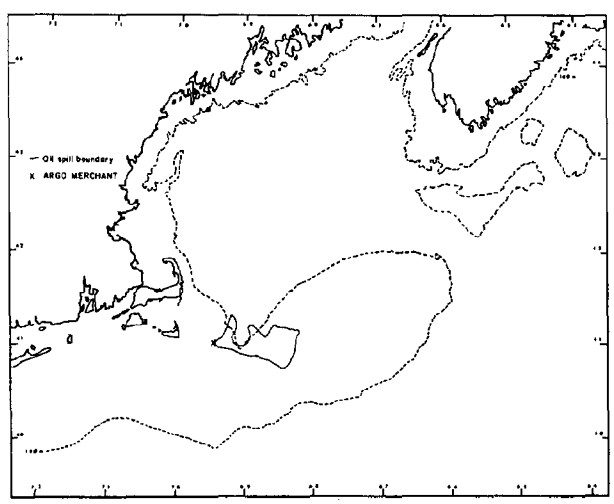

Figure 5a. *Map of Oil Slick, 21 December 1976.*

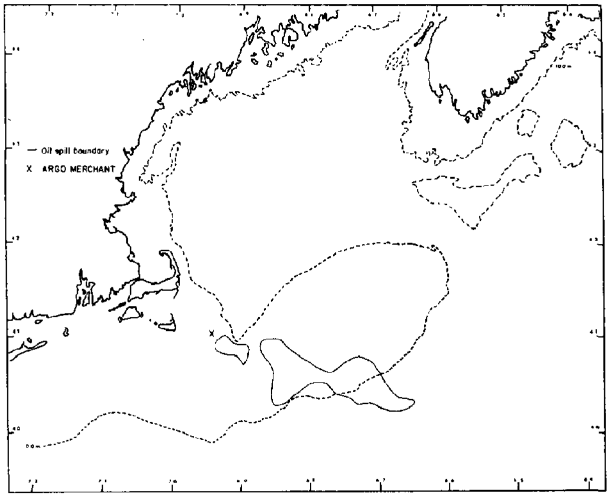

Figure 5b. *Map of Oil Slick, 27 December 1976.*

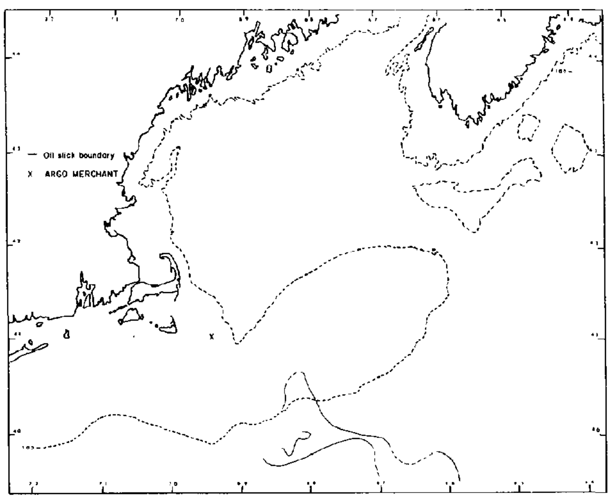

Figure 5c. *Map of Oil Slick, 2 January 1977.*

species within sight of the ship with the aid of binoculars, when the ship is moving on a fixed course and at a constant speed, 4 kts or faster, and when visibility is greater than 1 km. (Brown et al., 1975). This system of counting birds often results in inflated estimates of certain species because of repeated counts of the same ship-following individuals. All sightings of rare or infrequently occurring species were recorded. The species, number, age, behavior, and, when possible, the presence and degree of oiling were recorded.

From 20 December 1976 to 24 January 1977, the beaches of Nantucket Island and Martha's Vineyard were patrolled for stranded birds. Each bird found, whether dead or alive, was numbered, and the species, sex, age, date, location and degree of oiling were recorded.

Necropsies were conducted as follows:

(1) An external search for lesions and the degree of oiling was made.

(2) A mid-ventral incision was made from the sternum to the vent.

(3) Lungs, kidneys, brain and liver were examined for congestion.

(4) The digestive tract was examined for food and parasites.

(5) The remainder of the respiratory tract was examined for blockage.

(6) Lung, kidney, and liver sections from all specimens were preserved in 10% buffered formalin. Other tissue samples (e.g. heart, intestine, gizzard) were taken from some specimens. All tissue samples collected were placed on file at the Biological Science Center at Boston University.

Results

Pelagic Observations. From the USCGC *Vigilant,* 1120 birds of 13 species were recorded (U.S. Dept. of Comm./NOAA, 1977) with daily total counts ranging from 28 to 261 birds. Almost 92% of the total number of birds counted were gulls, Great Black-backed *(L. marinus),* Herring *(L. argentatus),* and Black-legged Kittiwake *(R. tridactyla);* 6% were Gannets *(Morus bassanus);* 1% were fulmars *(Fulmarus glacialis)* and alcids *(Alcidae).* The incidence of oiling was highest for Great Black-backed and Herring Gulls, at 41% and 59%, respectively, of the total for each species, but was lower for Gannets (12%) and kittiwakes (9%).

In January a total of 146 acceptable 10-minute watches were made during three cruises to Nantucket Shoals and Georges Bank. Effort, i.e. the number of acceptable 10-minute watches made per 30'N x 30'W latitude/longitude block, is indicated in Figure 1. Maps indicating the average number of individuals counted per acceptable 10-minute watch for fulmars, Great Black-backed Gulls, Herring Gulls, and Kittiwakes are compiled in Figures 2a-d. Maps indicating 10'N x 10'W blocks in which there was at least one sighting of large auks *(Alca torda* or *Uria* spp.) and Dovekies *(Plautus alle)* are illustrated in Figures 3a-b. Using all acceptable 10-minute watches, percentages of the number of visibly oiled birds to total number of each species inspected for oiling were mapped for fulmars and the three gull species in each 30'N x 30'W latitude/longitude block surveyed (Figures 4a-d). The results indicated a higher number of fulmars and gulls outside of the oil slick area but a larger proportion of visibly oiled birds near the grounded tanker and oil slick track. The movement and area covered by the oil on 21 and 27 December 1976 and 02 January 1977 are indicated in Figures 5a-c (U.S. Dept. of Comm./NOAA, 1977).

A total of 47 large auks was recorded in 16 sightings (Figure 3a). All sightings, except one, were made within 40 nautical miles of the wrecked tanker. Identification of the large auks to species was difficult because they were usually seen sitting on the water and observation was often hampered by rough seas and strong winds. No visibly oiled large auks were seen on any of the January cruises, but most were not observed at a range that would permit detection of oil on the underparts. A total of 91 Dovekies was recorded in 19 sightings (Figure 3b). Most Dovekie sightings were made on the Northern Edge and Northeast Peak of Georges Bank, away from the spill. In a flock of 54 Dovekies seen at 40° 42'N, 66° 51'W on 6 January 1977, 10 were visibly oiled. Two additional oiled Dovekies were sighted at 41° 21'N, 66° 57'W, on the same day.

Table 1. Numbers of Birds, by Species, Collected from Beaches at Nantucket Island and Martha's Vineyard, 20 December 1976 to 24 January 1977.

Species	*Live*	*Dead*	*Total*	*Percent of Total*
Common Loon	11	21	32	18
Red-throated Loon		1	1	1
Gannet	1	1	2	1
Grebe sp.		1	1	1
Double-crested Cormorant		1	1	1
Cormorant sp.	1		1	1
Common Eider	2	3	5	3
White-winged Scoter		1	1	1
Common Scoter		1	1	1
Great Black-backed Gull	2	29	31	17
Herring Gull		15	15	8
Bonaparte's Gull		1	1	1
Black-legged kittiwake	1	1	2	1
Razorbill	16	10	26	14
Common Murre	32	17	49	27
Thick-billed Murre	3	7	10	6
Murre sp.		1	1	1
Dovekie		1	1	1
	69	112	181	

Beached Bird Survey. Birds started to wash ashore on Nantucket Island 5 days after the tanker went aground. From 20 December 1976 to 24 January 1977, 173 birds were collected from beaches at Nantucket Island (Cardoza, 1977a, 1977b) and 8 oiled birds washed ashore on Martha's Vineyard (Gus B. David, personal communication). A total of 69 live and 112 dead birds of 16 species were handled (Table 1). From the total number of birds found during the beached bird surveys, it appears that alcids (49%), gulls (27%), and loons (19%) sustained the greatest impact.

Of the 181 birds retrieved from the beaches, 15 specimens were examined internally. Results from the necropsies are summarized in Table 2. Pathology findings indicated three conditions common to all specimens:

(1) all were underweight as determined by exposure of the keel

(2) all lacked a layer of body fat

(3) none had food in the digestive tract.

The lungs and kidneys were the vital organs most seriously affected. The lungs in 7 birds had hemorrhaged, probably due to blockage of the capillary spaces by ingested oil, and 2 specimens had lipid pneumonia. These findings are similar to those made by Hartung and Hunt (1966) on waterfowl. Two types of renal pathology were observed. The first consisted of cellular debris apparently causing a blockage of Bowman's capsule, and the second involved a precipitation of urates in the tubules, which again resulted in blockage of urine flow. The result in either case was the same; the bird was unable to filter waste products from the blood, which resulted in uremic poisoning. No oil was found in the kidneys, but the digestive tract would have broken down the oil into other by-products, thereby making the oil macroscopically undetectable. Since these findings match the descriptions of oil-induced kidney changes studied by Hartung and Hunt (1966), we assume that the pathologies observed are oil-related. It is possible, however, that similar results could have been produced by dehydration. There were three cases in which both the lung and kidney were congested, but neither organ alone appeared to be sufficiently affected to cause death.

One Common Murre *(Uria aalge),* which had only traces of oil on its plumage, was not a victim of an oil-related death, but had a chronic infestation of parasitic flukes in the kidney and digestive tract. No taxonomic identification of the parasites was made.

Discussion

To best determine the effect of an oil spill on pelagic birds, sea observations are essential. Beached bird surveys give a low estimate of the actual harm done, but more importantly, beach surveys do not provide any data to determine the potential threat presented by an oil spill. Purely marine species, such as auks and fulmars, do not come ashore unless they are severely oiled (Bourne, 1968). Many partially oiled birds remain at sea and eventually die there, and because the water-repellent properties of the plumage are destroyed, the birds become waterlogged and sink (Clark, 1968). After the *Argo Merchant* went aground, several thousand surface and seabed drifters were released at various positions near the tanker (U.S. Dept. of Comm./NOAA, 1977). No surface drift cards were found and only 1 seabed drifter was recovered on shore. Because of adverse tidal currents and westerly prevailing winds at that time, the probability of birds drifting ashore to Cape Cod and the islands was remote. We suspect that the small number of birds that went ashore had made an active effort to get there after being oiled.

Table 2. Summary of Pathology Findings.

		Number of Specimens with:				
Species	*Sample Size*	*Hemmorrhagic Lungs*	*Pneumonia*	*Kidney Blockage*	*Kidney/Lung Congestion*	*Parasites (Chronic)*
Common Loon	5	2	1	2	0	0
Great Black-backed Gull	2	2	0	0	0	0
Herring Gull	3	2	0	0	1	0
Common Murre	4	1	0	1	1	1
Thick-billed Murre	1	0	1	0	0	0

Of the 181 birds that did come ashore, alcids (49%) were the most numerous species. Sea observations, however, indicate that gulls were the most affected species. There are two reasons for the variation between the pelagic and beached bird observations. The first is that few alcids were observed during the cruises in January, while unprecedented sightings of alcids, such as 800 Razorbills, 4000 Thick-billed Murres, and an additional 1200 unidentified alcids at Race Point, Provincetown (E. Mass. Bird Observer, 1977), were made along the Massachusetts coast. Since the alcids were close to shore, those affected by the spill had a higher probability of coming ashore than did more distant birds. Second, the larger numbers of fulmars and gulls were associated with trawlers fishing on the Northeast Peak and Northeast Channel (Figures 2a,b,d). During the counts, concentrations of several thousand individuals were estimated for each of the following species; fulmar, Great Black-backed Gull, and kittiwake. Counts made in the vicinity of foreign fishing activities on the continental slope south of Massachusetts and Rhode Island averaged 30-100+ Great Black-backed and Herring Gulls but 0-10 fulmars per watch. In contrast, near the grounded tanker and oil slick track, 0-30 fulmars or gulls were recorded per watch.

The percentage of visibly oiled birds was often greater near the tanker or oil slick track than in surrounding waters. From 3 to 30 percent of fulmars observed on Nantucket Shoals, Great South Channel, and western Georges Bank were visibly oiled. No oiled fulmars were recorded in the other areas surveyed. Percentages of oiled gulls were greatest on Nantucket Shoals, Great South Channel, and western Georges Bank, but oiled gulls were observed in other areas. The tendency of large gulls and kittiwakes to follow ships probably caused the wide dispersal of oiled individuals, thus reducing the probability of their coming ashore when sick or dying.

Beached bird surveys provide the only specimens which can be examined to determine the manner in which the birds came in contact with the oil as well as the effects of oil on the birds. Loons and alcids were generally oiled on the belly, sides, and lower back (Cardoza, 1977a), indicating that the birds came in contact with the oil when resting on the water. Gulls were also oiled on the breast (Cardoza, 1977a) indicating that they may become oiled while feeding. Diving birds, such as loons and auks, are the species most vulnerable to oil spills because of the amount of time they spend resting on the water (Bourne et al., 1967; Hope-Jones et al., 1970; Greenwood et al., 1971; Brown et al., 1975).

As stated previously, the lungs and the kidneys were the organs most seriously affected. The most likely route for oil entering the lungs is through the glottis, either by leakage or through inhalation. If, for example, the bird chokes or coughs while preening oiled feathers, the oil could enter the trachea. Once oil is in the lungs, it becomes lodged in the parabronchi where it is surrounded by erythrocytes, lymphocytes, and neutrophils. Blockage of some parabronchi probably causes an increase in blood pressure in other parabronchi and the combination of restricted circulatory flow and increased blood pressure in the lungs results in hemorrhaging which can kill the bird.

The kidney pathology matches the description of oil-induced changes from Hartung and Hart (1966), but dehydration would give similar results. By destroying the water-repellent properties, oil on the plumage could have impaired the birds' ability to swim and/or catch food. Since all of the birds were underweight and had no food in the digestive tract, it is possible that dehydration could have occurred from a lack of dietary derived water.

Acknowledgments

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The *Argo Merchant* Oil Spill and the Fisheries

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Abstract

The impact of oil spilled from the *Argo Merchant* on fish stocks has not been catastrophic. No evidence of large scale mortalities of juvenile or adult fish has been observed in the 12 months (Jan.-Dec. '77) following the spill. There has been, however, evidence of oil contamination in fish, shellfish, and zooplankton populations in the area of the spill. Mortalities of developing cod and pollock embryos contaminated with oil were observed. A few adult fish (<5% of those examined) had apparently ingested *Argo*-like oil. The dominant zooplankton species in the area of the spill was the copepod *Centropages typicus,* which is an important food of larval and adult fish. Large numbers of this species were contaminated with petroleum hydrocarbons similar to No. 6 fuel oil, indicating that an important pathway in the food web of the Nantucket Shoals-Georges Bank ecosystems was impacted. The long-term effects of the *Argo* oil on the marine ecosystem will be difficult to assess. A more significant problem concerns the chronic background levels of petroleum hydrocarbons present in the surface waters inhabited by fish eggs and larvae.

Introduction

The tanker *Argo Merchant* ran aground on Nantucket Shoals 15 December 1976. By 8 February 1977 approximately 7.7 million gallons of No. 6 fuel oil had been released into the waters of the Continental Shelf. In the immediate vicinity of the wreck, concentrations of petroleum hydrocarbons up to 250 ppb were detected. Heavy winter winds and seas contributed to the fragmentation of large "pancakes" viewed in the immediate vicinity of the *Argo* following the breakup of the vessel on 21 December. Available evidence from Coast Guard overflights of the spill zone indicated that within 40 days the oil was carried in small "pancakes" and "streaks" under the influence of prevailing winds and currents away from shore and in a general southeasterly direction off the Continental Shelf into slope and oceanic water. The impact of the *Argo* oil on the fisheries during its relatively limited residence time is the subject of the present report.

To date no comprehensive study has been carried out on the effects of oil on the productivity of fish populations on the northeast Continental Shelf. In fact, with the exception of the *Torrey Canyon* Spill, the Santa Barbara, and more recently, the EKOFISK spills, most studies on the effects of oil on fish and shellfish have been concerned with the onshore or near-shore impacts on littoral organisms (Sanders, 1977). Sublethal effects of crude oil have been described for saithe, *Pollachius virens* (pollock), in the immediate vicinity of a grounded tanker off the Norwegian coast (Grahl-Nielsen et al., 1976). In experiments where salmon and saithe were exposed to a maximum of 50 μ gms EKOFISK crude oil/liter seawater, both species showed residues of petroleum hydrocarbons within 7 hrs of dosing. Following termination of dosing after 68 days, both species showed naphthaline levels comparable to those existing prior to dosing, indicating that at moderate dosage levels, effects are sublethal and reversible (Brandal et al., 1976).

Laboratory studies have shown that crude oil can damage developing fish eggs and cause high mortalities in cod, herring and capelin embryos (Kuhnhold, 1969, 1974; Johannessen, 1976). Also, the zooplankton food of fish larvae suffer high mortalities from exposures to crude oil in laboratory experiments (Mironov, 1969). Recent studies in large scale microcosms at the University of Rhode Island have also revealed that No. 2 fuel oil at levels of 100-150 ppb has dramatic negative effects on population numbers and physiological responses of copepods (S. Vargo, personal communication). In contrast, observations from collections made at sea have shown that zooplankters, particularly copepods, can ingest particles of oil and pass them through the gut without any observable negative effects (Conover, 1971, Parker, 1970). Some species of adult fish have been observed to avoid areas contaminated with oil. However, the more sensitive egg and larval stages are carried by the tides and currents and lack the ability to avoid oil spill areas. Bivalve shellfish (quahogs, scallops, mussels) are sedentary and have only limited capability to remove large amounts of petroleum hydrocarbons. They suffer significant mortalities in areas contaminated with oil (Blumer et al., 1970; Thomas, 1973; Jeffries and Johnson, 1975). Proper assessments of the impact of a major spill on the Continental Shelf require the combined effort of extensive sea sampling and experimental support studies.

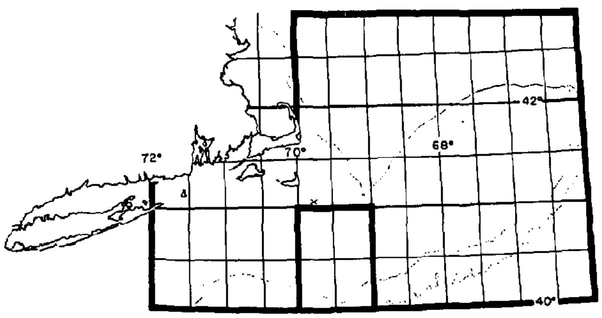

Figure 1. *Statistical areas examined for U.S. commercial catch data 1975, 1976, 1977. The small rectangle represents fishing grounds adjacent to the Argo wreck. The large rectangle represents ICNAF statistical subareas 5Ze and 5Zw. The Argo wreck site is marked with an X.*

Methods

Several data bases were used to evaluate the impact of *Argo* oil on the fisheries in the region of the spill including fish catches, zooplankton, ichthyoplankton, and neuston. Monthly catch data from commercial landings were compiled for the area in the vicinity of the wreck for 1975, 1976, and 1977. To allow for changes in the distribution of the stocks, catches from a wider area encompassing both Nantucket Shoals and Georges Bank were analyzed (Figure 1). Fisheries independent abundance information was obtained from the results of the spring and autumn bottom trawl surveys conducted as part of the Marine Resources Monitoring Assessment and Prediction Program (MARMAP) of the National Marine Fisheries Service. The surveys have been made continuously off the northeast coast for the past 15 years by the Northeast Fisheries Center (Grosslein, 1976) and represent a valuable time-series of comparable data (Figure 2).

Zooplankton and ichthyoplankton samples were collected with paired 60-cm bongo nets towed obliquely through the water column from just off bottom to the surface at 1.5 kts. Also, surface plankton was collected with a 0.5 m x 1.0 m neuston net towed at the surface at 1.5 kts. The dates and areas of collection are given in Table 1.

Information on the presence of *Argo* oil over the fishing grounds was obtained directly from the fishermen in two activities. The first was from an initial survey of fishermen in each of the principal ports of the northeast coast. Fishermen were interviewed at dockside by NMFS

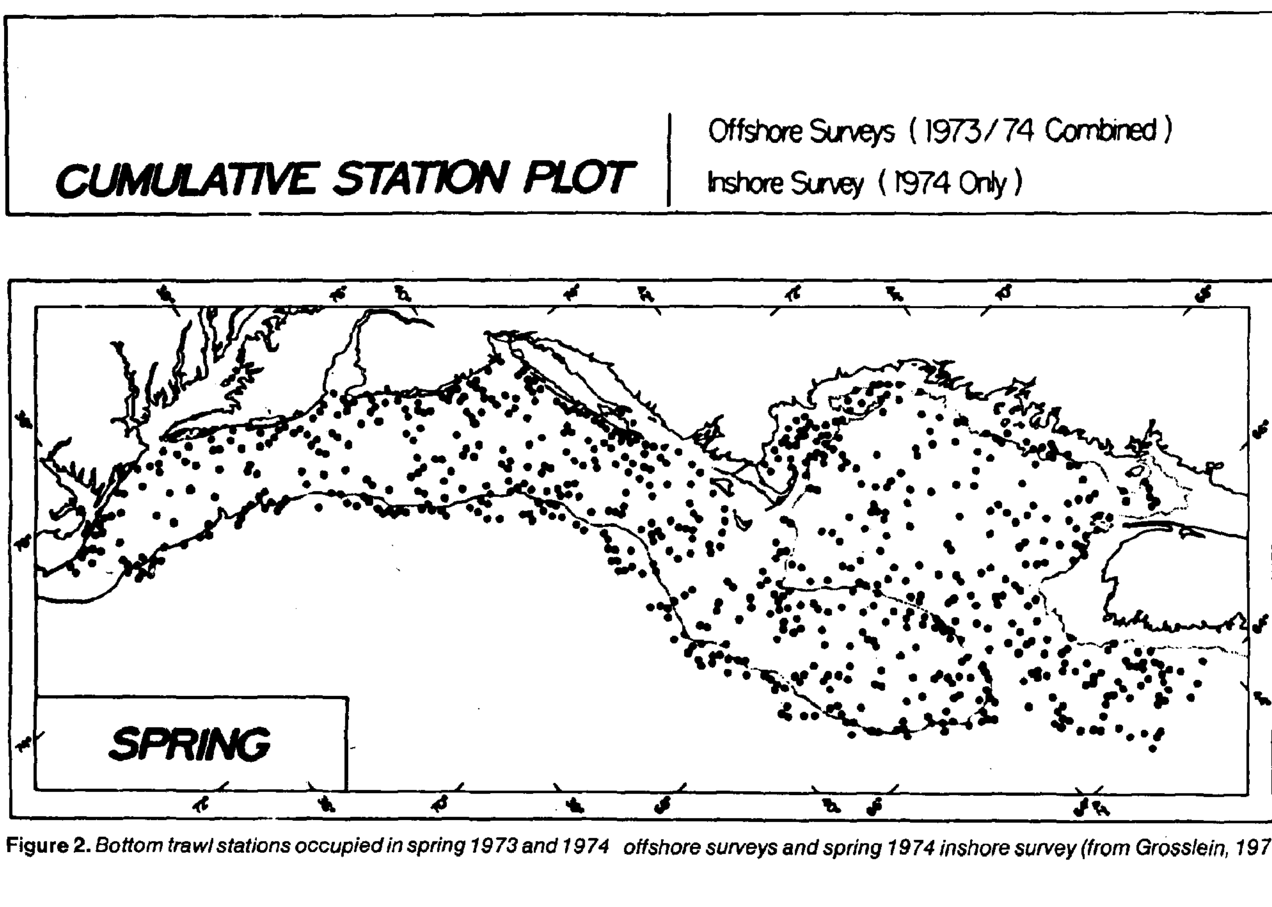

Figure 2. *Bottom trawl stations occupied in spring 1973 and 1974 offshore surveys and spring 1974 inshore survey (from Grosslein, 1976).*

Table 1. Dates and Areas of Sample Collections.

Vessel	*Date*	*Location of Sample Area*	*No. Samples Examined*
Delaware II, NMFS, NOAA	22-24 Dec. 1976	*Argo* area, Nantucket Shoals*	9
Delaware II, NMFS, NOAA	4-10 Jan. 1977	Nantucket Shoals, Georges Bank, Race Point* **	43
Mt. Mitchell, NOAA	12-26 Feb. 1977	Nantucket Shoals, Georges Bank	38
Endeavor, URI	22-27 Feb. 1977	Nantucket Shoals**	20
Wieczno, Poland	27 Feb.-6 Mar. 1977	Nantucket Shoals, Georges Bank* **	41
Gorlitz, GDR	3-15 Mar.; 15 Mar.-3 Apr. 1977	Southern New England, Nantucket Shoals, Georges Bank	22
Albatross IV, NMFS, NOAA	13 Apr.-14 May 1977	Nantucket Shoals, Georges Bank*	18
Nogliki, USSR	22 May-6 Jun. 1977	Southern New England, Nantucket Shoals, Georges Bank	34
Yubileiny, USSR	31 Jul.-15 Aug.; 17 Aug.-3 Sept. 1977	Southern New England, Nantucket Shoals, Georges Bank	33
Wieczno, Poland	4-24 Oct. 1977	Nantucket Shoals, Georges Bank	19
Argus, USSR	15 Oct.-10 Nov. 1977	Southern New England, Nantucket Shoals, Georges Bank	32

* *Cruise on which fish samples were collected.*

** *Petroleum hydrocarbon analysis of zooplankton samples from this cruise.*

personnel. In addition, observations of 5 groups representing several hundred vessels, captains, and deck hands were collated and analyzed by employees of Development Sciences Inc. of Barnstable, Mass. The results of this survey were used in the analysis.

The Fisheries of Nantucket Shoals and Adjacent Waters. NEFC Port Agents attempted to assess the impact of the *Argo Merchant* oil spill on the daily activities of the commercial fishermen. In New England approximately 900 direct interviews were made from a total of 4,000 fishing trips between 21 December and 30 January, at the ports of Portland, Rockland, Gloucester, Boston, and New Bedford, Massachusetts; and Newport and Pt. Judith, Rhode Island. Of 26 interviews conducted where evidence of the oil spill was noted during that period, 5 (20%) indicated direct loss of catch, fouling or loss of gear. The other 21 (80%) reported "oily" birds. All of these incidents occurred in the area to the southeast of the site of the *Argo Merchant* at locations associated with fishing operations.

Specific problems were loss of gear, fouling, or loss of catch. A scalloper fishing very near the wreck area had his catch and gear fouled by an oil slick; the catch from that tow was discarded as unmarketable. Captains of two vessels, fishing American lobster on the edge of the Continental Shelf, believe that oil fouling of inflatable buoys caused a deterioration of air valves resulting in a loss of these buoys and consequently the gear they marked. The crew's clothing became fouled during handling the gear. One lobster fishing vessel had its gear in the immediate area of the oil drift and, as a result, had to change over the water circulation system from a continuous to a closed one, i.e., instead of taking in water from the area of the oil drift and contaminating the catch, water from a clean area was used and circulated within the vessel's holding system. No reports of adverse effects of *Argo* oil were made by foreign fishing vessels.

In a draft report (Development Sciences, 1977), a consortium of 5 non-profit fisheries organizations initiated and carried out a program aimed at determining the impact of the oil on the fish of the Nantucket area. The 5 groups represent several hundred vessels, captains and deck hands. The activity was supported by the Office of Technology Assessment and coordinated by Development Sciences of Barnstable, Mass. The fishing fleet reported seeing oil slicks associated with *Argo Merchant* until March 30 with major concentrations observed before 10 February. The most significant impact reported by fishermen was the hundreds of oiled birds observed during the period from January through April. They found no evidence of oil on the bottom. The only oil damage reported was limited to the observation of oil in the

Table 2. Abundant Fish Species in the Nantucket Shoals - Georges Bank Area.[a]

Spill Zone	Metric Tons Apr-Dec. 1975	Metric Tons Jan-Dec. 1976	Total Area	Metric Tons Jan-Dec. 1975	Metric Tons Jan-Dec. 1976
Sea scallops	2086	5753	Yellowtail flounder	16,986	14,515
Cod	5260	5742	Cod	15,227	14,213
Winter flounder	1932	1547	Sea scallops	7,556	14,725
Yellowtail flounder	1203	1333	Menhaden	7,168	5,718
Pollock	333	641	Silver hake	6,584	6,407
Haddock	369	416	Winter flounder	5,955	4,601
Silver hake	282	175	Sea herring	4,041	541
Windowpane	239	358	Haddock	3,986	2,894
Redfish	209	119	Redfish	3,113	2,143
Summer flounder	175	314	Pollock	2,979	3,843
American plaice	29	58	Summer flounder	1,943	3,418

[a]These species represent 94-99% of the total catch in each of the two years.

stomach of two codfish shortly after the spill.

We examined commercial catch statistics from statistical areas adjacent to the wreck site. The catch data from the spill zone came from an area of approximately 3,600 square miles. Recognizing that fish undergo migration for feeding and spawning, we examined catch statistics of a larger area. The broader area examined covered approximately 54,000 square miles (Figure 1).

We examined the catches for two years (1975, 1976) prior to the spill to identify the most abundant species in the spill area. The three most frequently caught species are: cod, sea scallops and winter flounder (Table 2). A summary of monthly commercial catch data for the abundant species is given for both the spill area and the Nantucket Shoals-Georges Bank area in Figures 3 and 4. Catches of cod and scallops are highest in 1977. Winter flounder catches are similar in each of the three years. No downward trends in abundance were evident (Figure 3). In the total area examined, cod, scallops, and yellowtail flounder were the most frequently caught species. Cod and scallop catches were higher in 1977 and yellowtail flounder landings were similar among the three years (Figure 4). These data are unweighted catches, and are used here as only an indication of catch trends in the area. No allowance has been made for changes among the three years in fishing effort.

Bottom Trawl Survey. The semi-annual bottom trawl surveys conducted by NEFC monitor changes in abundance of the principal fish stocks in the area. Major changes in the abundance of the stocks prior to the *Argo Merchant* spill were the result of the interaction between intensive fishing and naturally occurring environmental fluctuations. In combination, these events have reduced the fish biomass substantially from former abundance levels in the 1950's and early 1960's (Clark and Brown, 1977). Against this dramatic change in biomass, we are attempting to sort out the impact of *Argo* oil on the stocks in the vicinity of the spill.

We have seen no dramatic changes in the stocks of yellowtail flounder, cod, sea scallops, or winter flounder from 1975 through 1977. The catches of the four species for spring and fall of '75, '76, and '77 are plotted in Figure 5a-h. It should be noted that this is preliminary data and the variability inherent in the data has not been analyzed, but no downward trends in abundance were observed. Although these four species were abundant around the wreck site, they are widely distributed over the survey area, with concentrations on the northeast part of Georges Bank; the wide distribution of the species enhances the probability of survival.

Ichthyoplankton. At the time of the spill, six species of fish larvae were in the collections: sand launce, cod, pollock, rockling, hake, and herring. Of these species, only sand launce was abundant (Tables 3a and b). Other larvae were rare.

The abundance of sand launce larvae decreased sharply at the two sampling stations within the spill area and showed an increase at the periphery of the oiled waters in the bongo tows, but decreased in the neuston samples (Figure 6). However, the reasons for the decrease are not clear. It may have been associated with the negative impact of the oil on the viability of larvae, or it may have been a reflection of the "patchiness" characteristic of larval fish distributions. The sand launce, while

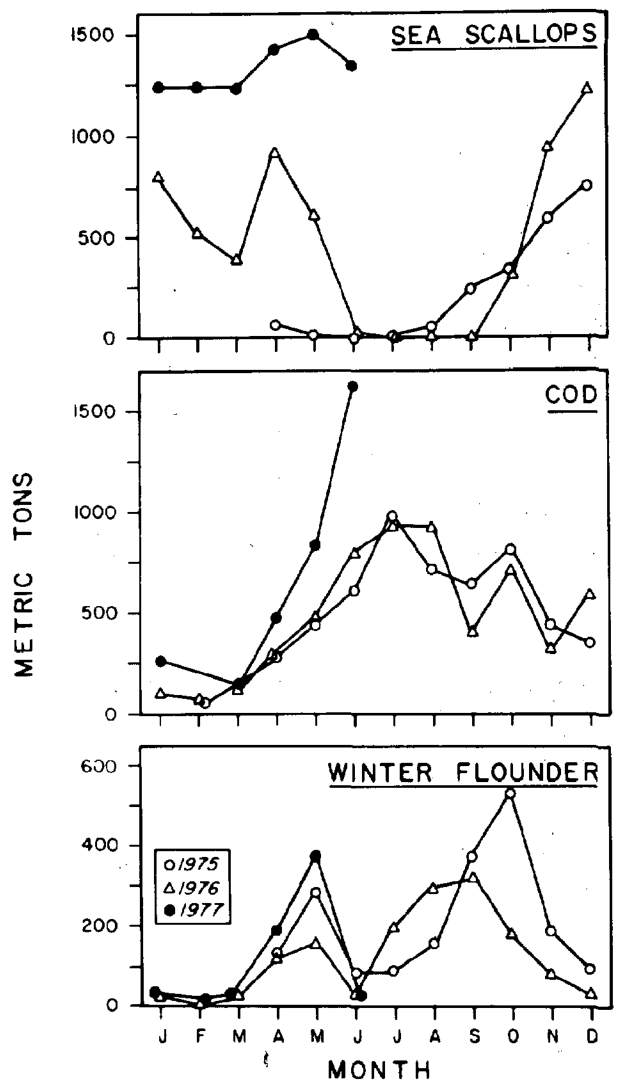

Figure 3. *Monthly U.S. commercial catch of winter flounder, cod, and sea scallops in the Argo Merchant spill area for 1975, 1976, 1977.*

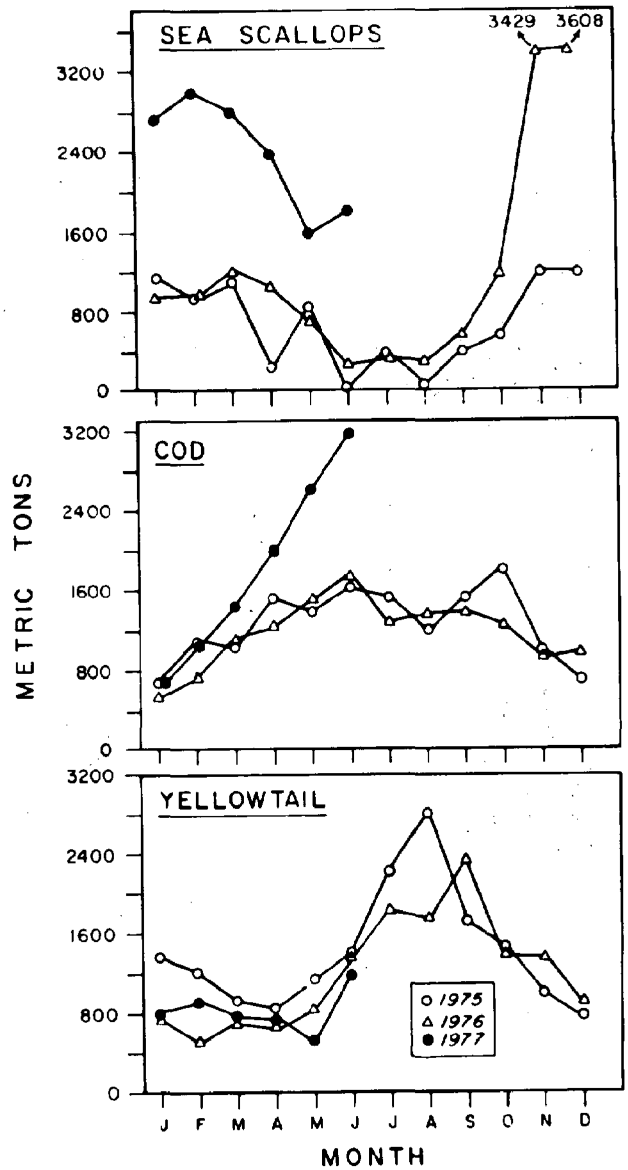

Figure 4. *Monthly U.S. commercial catch of yellowtail flounder, cod, and sea scallops in the Nantucket Shoals-Georges Bank area for 1975, 1976, 1977.*

not important in the commercial fishery, is a key species in the ecosystem. It is the basic food of predatory fish including cod, haddock, silver hake, as well as marine mammals including porpoises and whales. Data from prior years ('73, '74, '75, '76) has shown abundances of sand launce in the southern New England-Mid Atlantic Bight areas increasing every year since 1973. Preliminary analysis of the 1977 data suggests this trend is continuing.

There is evidence that *Argo* oil caused cytogenetic mortalities to fish eggs. Mortality among pollock eggs increased significantly in the areas of the spill and some mortality of cod eggs was evident (Longwell, 1977). Also, laboratory experiments have shown that *Argo*-type oil is toxic to developing cod eggs and can cause high levels of embryo mortality (Kuhnhold, 1977). Whether *Argo* oil has had a negative impact on new recruits to cod, pollock, and scallop populations of the Nantucket Shoals area remains an open question. Additional ichthyoplankton, bottom trawl and shellfish surveys scheduled for 1978 and 1979 by NMFS should provide data sufficient for making a more complete evaluation of any long-term effects.

Zooplankton. The communities of zooplankton in the vicinity of the oil spill were described in the NOAA (1977) report "The *Argo Merchant* Oil Spill." Significant contamination was found in copepods subsequent to the spill. The dominant copepod in the area of the spill was *Centropages typicus*, a food of both larval and adult fish. Large numbers of *C. typicus* were contaminated with hydrocarbons similar to No. 6 fuel oil indicating that an

YELLOWTAIL FLOUNDER

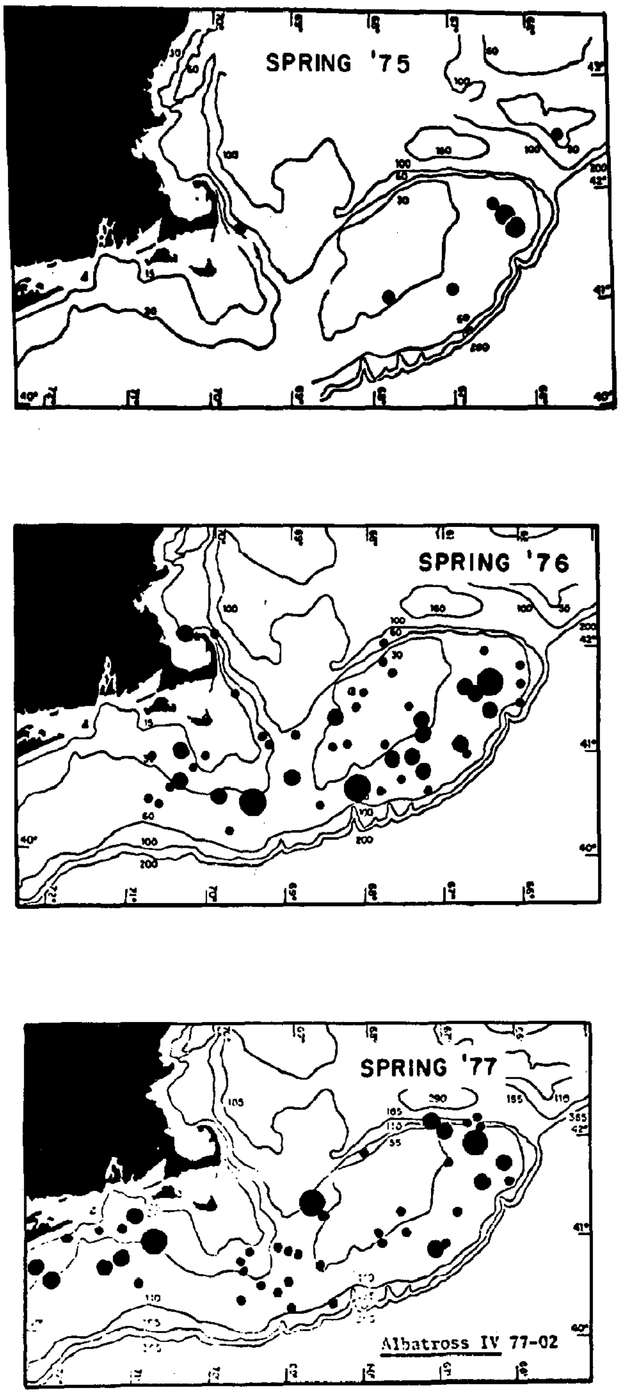

Figure 5a. *NEFC bottom trawl catches of yellowtail flounder for spring 1975, 1976, 1977. Large circle, 10-20 kilos; medium circle, 5-10 kilos; small circle, <5 kilos.*

YELLOWTAIL FLOUNDER

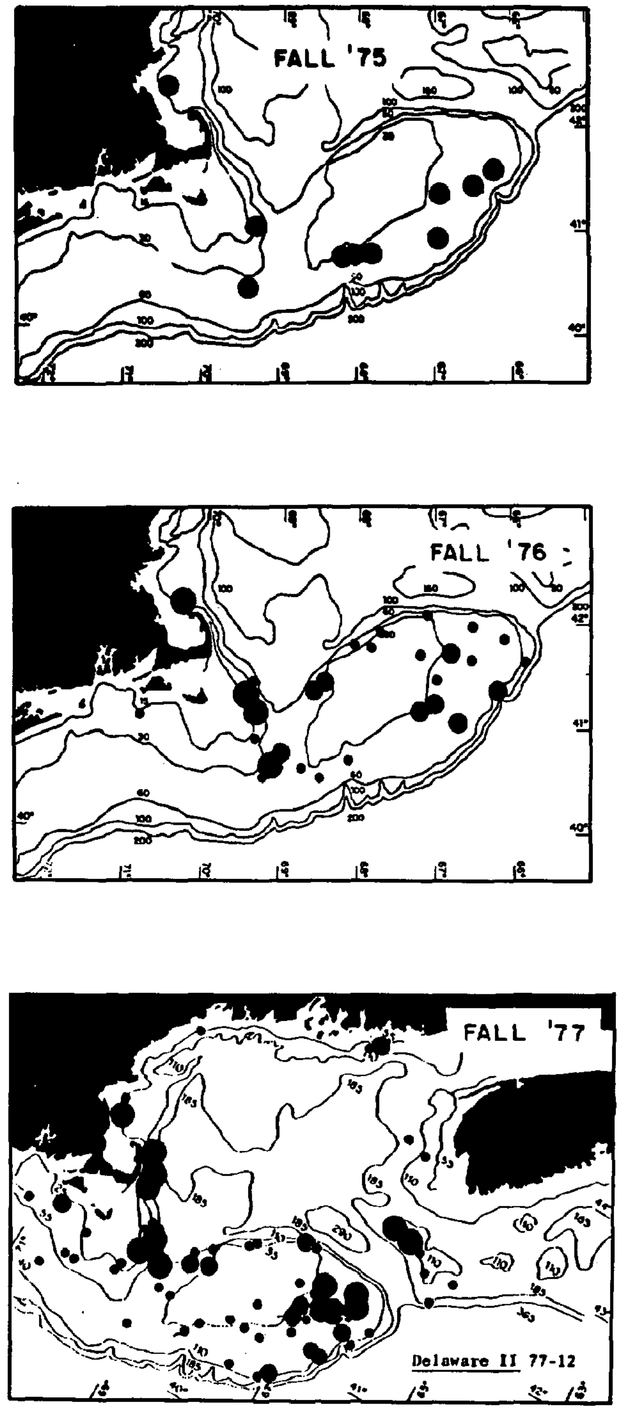

Figure 5b. *NEFC bottom trawl catches of yellowtail flounder for fall 1975, 1976, 1977. Large circle, 10-20 kilos; medium circle, 5-10 kilos; small circle, <5 kilos.*

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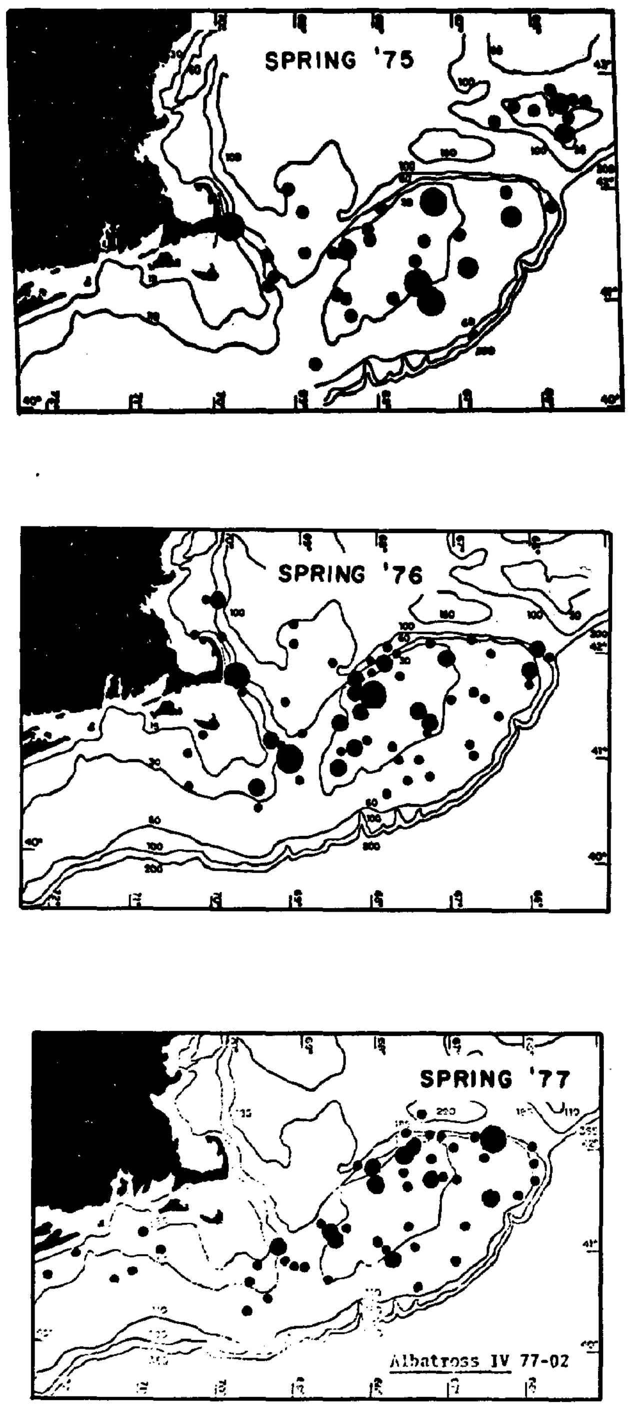

Figure 5c. *NEFC bottom trawl catches of cod for spring 1975, 1976, 1977. Large circle, 50-400 kilos; medium circle, 20-50 kilos; small circle, <20 kilos.*

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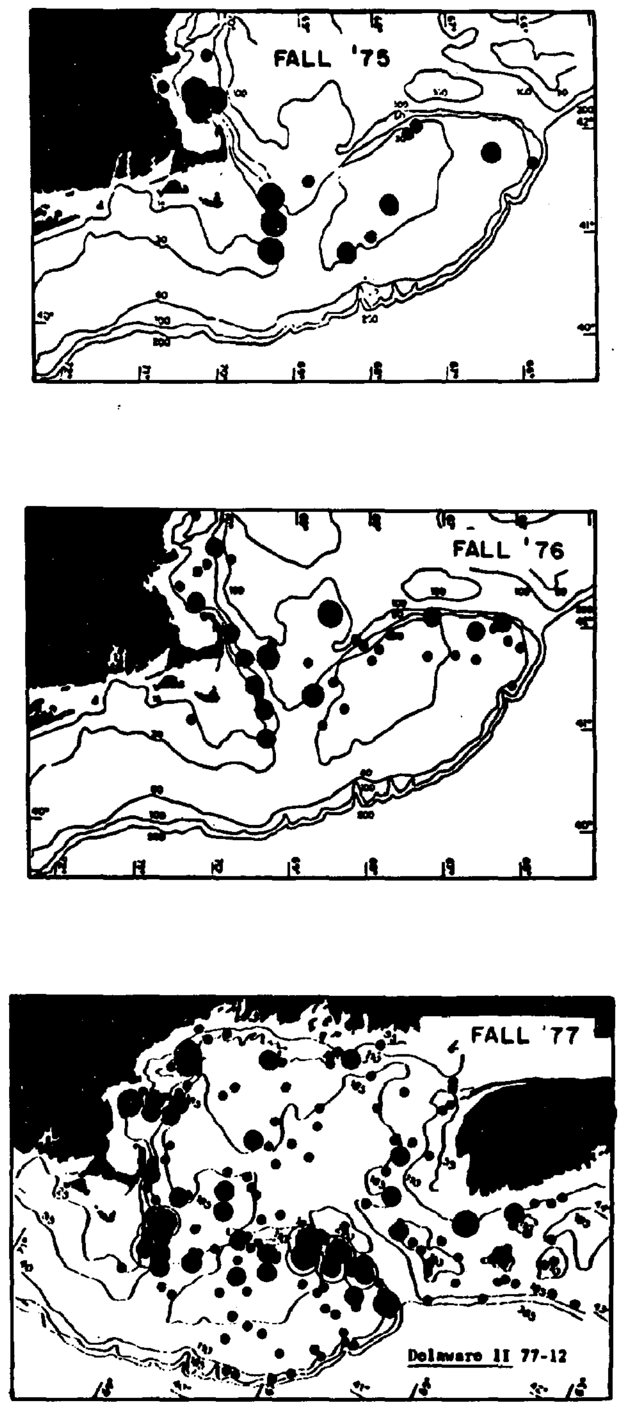

Figure 5d. *NEFC bottom trawl catches of cod for fall 1975, 1976, 1977. Large circle, 50-300 kilos; medium circle, 20-50 kilos; small circle, <20 kilos.*

SEA SCALLOP

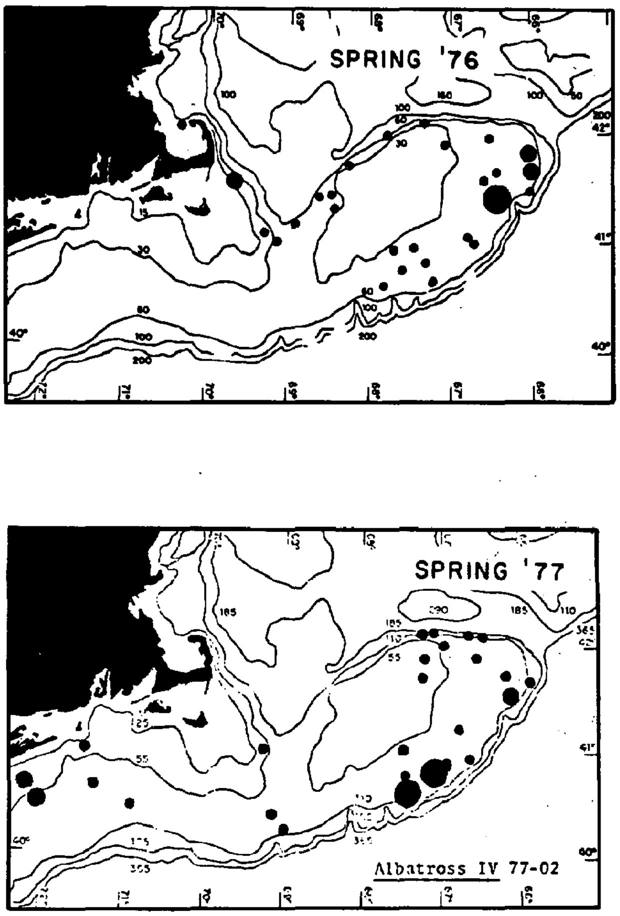

Figure 5e. *NEFC bottom trawl catches of sea scallops for spring 1976, 1977. Large circle, 100-300 scallops; medium circle, 20-100 scallops; small circle, <20 scallops.*

important component of the food web was impacted. When oil droplets removed from the alimentary tracts of *C. typicus* were examined for petroleum hydrocarbons using gas chromatography, the resulting chromatograms were similar to chromatograms of oil from the *Argo Merchant* (Kuhnhold, personal communication).

Four zooplankton samples from a time-series collected from December 1976 through November 1977 were sent to the NOAA Analytical Laboratory, Seattle, Wash., for hydrocarbon analysis. The samples analyzed were from three cruises conducted in January through

SEA SCALLOP

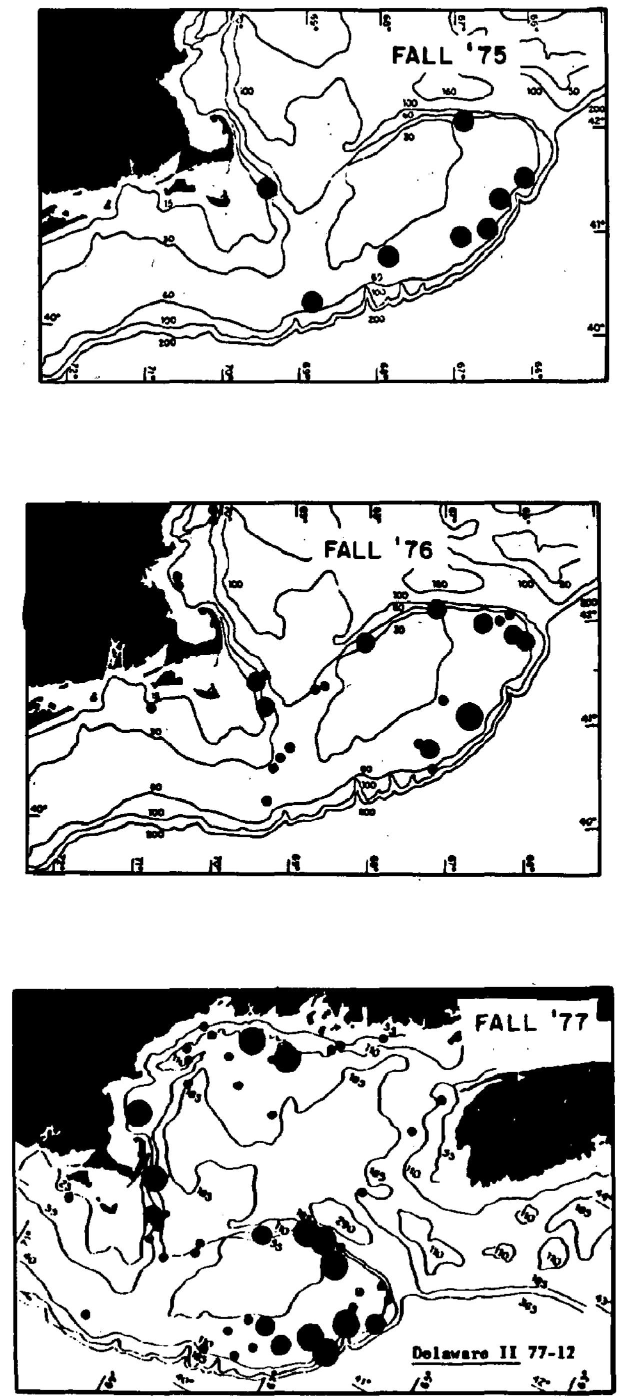

Figure 5f. *NEFC bottom trawl catches of sea scallops for fall 1975, 1976, 1977. Large circle, 50-700 scallops; medium circle, 20-50 scallops; small circle, <20 scallops.*

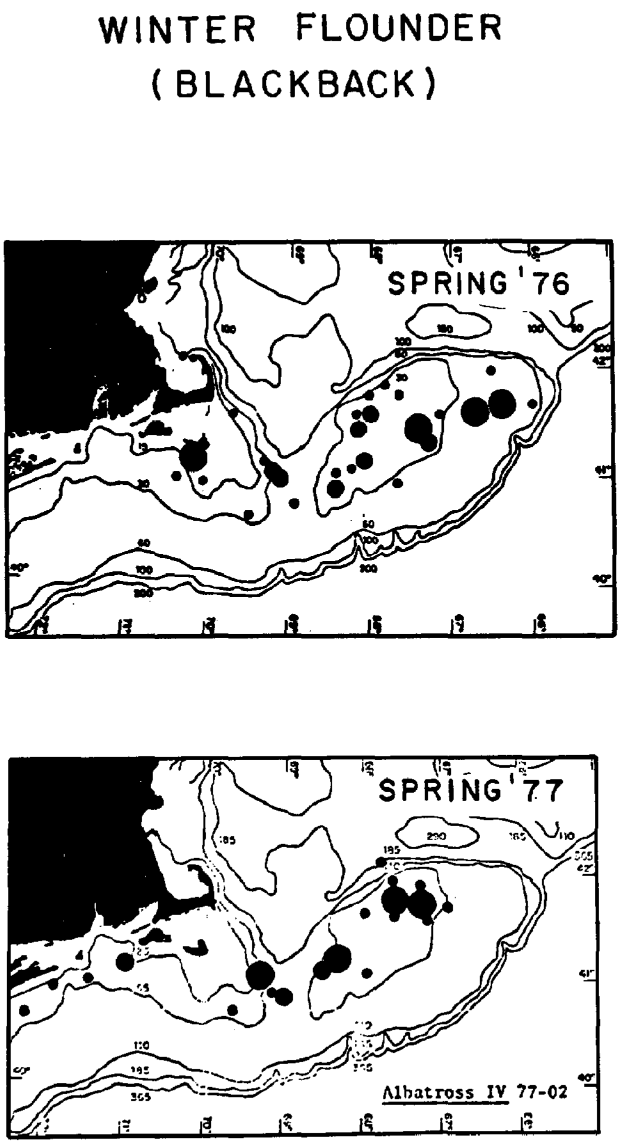

Figure 5g. *NEFC bottom trawl catches of winter flounder for spring 1976, 1977. Large circle, 10-125 kilos; medium circle, 5-10 kilos; small circle, <5 kilos.*

March 1977. No other samples from the time series were sent. Of the samples analyzed in Seattle, one sample taken on *Endeavor* Cruise 005 in February (41° 01'N, 69°31'W), west of the *Argo* bow section, contained saturated hydrocarbons which closely resembled the *Argo Merchant* cargo hydrocarbons, suggesting that the *Argo* could have been the source of contamination. Polak (personal communication) using a U-V fluorescence technique also found *Argo*-type oil in zooplankton from the spill site in February. The sample from the January cruise taken southwest (40°50'N, 69°35'W) of the wreck did not give a

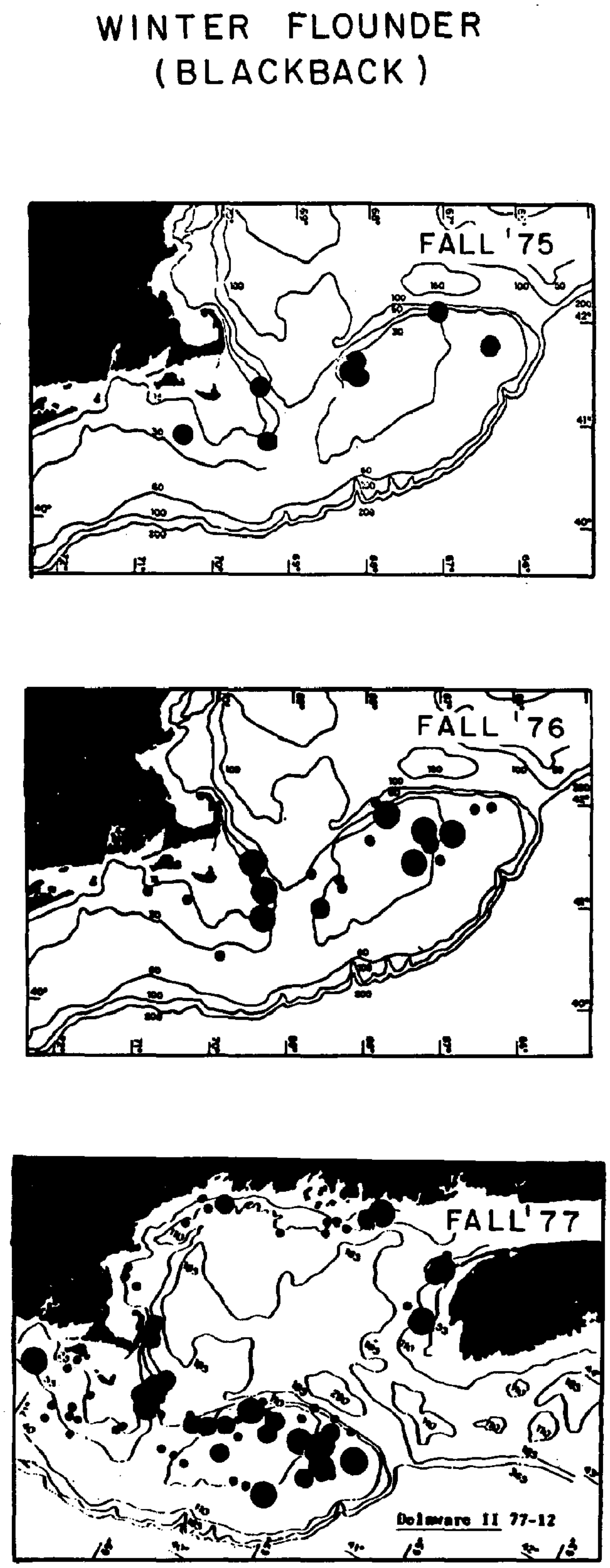

Figure 5h. *NEFC bottom trawl catches of winter flounder for fall 1975, 1976, 1977. Large circle, 10-125 kilos; medium circle, 5-10 kilos; small circle, <5 kilos.*

Table 3a. Numbers of Fish Eggs and Larvae per 1000 m^3 Collected in the Area of the *Argo Merchant* Oil Spill, Dec. 1976.

		Fish Larvae/ 1000 m^3		*Fish Eggs/ 1000 m^3*	
Station Number	*Species*	*61 cm Bongo .505*	*1 x 5 m Neuston .505*	*61 cm Bongo .505*	*1 x 5 m Neuston .505*
4	*Clupea harengus*	14			
	Ammodytes americanus	12,417	4,062		
	Gadus morhua			612	182
	Pollachius virens			86	5
5	*A. americanus*	21,197	2,172		
	G. morhua		1	72	23
	P. virens			95	20
	Enchelyopus cimbrius		1		
6	*C. harengus*	3			
	A. americanus	6,475	1,752		
	G. morhua			8	14
	P. virens	20	1	8	9
	Urophycis sp.		1		
7	*A. americanus*	2,967			
	G. morhua	7		11	
	P. virens			72	
8	*A. americanus*	7,857	41		
	G. morhua			30	18
	P. virens			1,439	826
9	*A. americanus*	41,184	222		
	G. morhua			317	217
	P. virens			36	188

high correlation with *Argo* oil. In the third and fourth samples from a subsequent cruise located east and east-southeast of the wreck (40°54'N, 69°14'W and 41°03'N, 68°59'W) in later February-March, no oil was found.

Hydrocarbon Analysis of Fish and Invertebrates. On February 1, 1977, a total of 66 specimens in 22 samples including 7 fish species (cod, haddock, red and silver hake, windowpane, winter and yellowtail flounder) and 3 invertebrate species (sea scallop, lobster and sand dollar) which were collected on *Delaware II* 76-13 and 77-01 cruises were sent to Dr. William MacLeod at the NOAA National Analytical Facility, Seattle, Washington, for hydrocarbon analysis. Three individual fish or invertebrates of the same species were pooled to constitute a single sample. Stomachs suspected of having oil content were analyzed separately.

A total of 9% of the fish had oil in their stomachs, but only 4.5% of that resembled *Argo Merchant* cargo. Four and a half percent of the samples had detectable amounts of fuel oil in the flesh, but this did not match well with *Argo Merchant* oil, indicating that these fish had been exposed to other sources of petroleum contamination. A summary of the incidence of fuel oil in the fish and shellfish samples is given in Table 4.

MacLeod reported that his results are not consistent since some of the oil residues were found in fish from potentially contaminated areas and others are from stations outside of the area overrun by the oil slick. For example, winter and windowpane flounders from Station 3, *Delaware II* Cruise 77-01, both showed oil in stomach and flesh even though they were taken close to shore off Nauset Light, Cape Cod, well away from the oil spill. On the other hand, the only fish specimen observed to have oil on it, a winter flounder from Station 4, showed no traces of oil in the stomach or in the flesh (Figure 7).

To determine if *Argo Merchant* oil was assimilated into the flesh over a period of time an additional 24 samples of fish and shellfish were sent to Dr. MacLeod on 30 June 1977. The seven fish species array was the same except no windowpane flounder were included and a sample of little skate was sent. The invertebrates included hermit crabs, *Cancer* sp., ocean quahogs and sea scallops. These samples were collected on *Wieczno* 77-01, 18 February-6 March 1977, and are presently being analyzed.

Neuston Series. We examined neuston samples through an annual cycle in the spill area from November 1976 through November 1977 (11 cruises) to determine the extent of oil contamination. We qualitatively estimated the amount of particulate oil and tar in 332 samples. Of this number, 36% were contaminated (Table 5). This is not surprising in view of previous work conducted by NEFC in the area. The level of oil and tar contamination in neuston samples taken between Virginia and Cape Cod ranged between 0.05 and 1.04 mg/m^2 in winter of 1973 and between 0.18 and 0.77 mg/m^2 in summer of 1972 (Sherman et al., 1974). Of an additional 382 neuston samples examined from the MARMAP/U.S. Coast Guard cooperative monthly neuston sampling program (March 1975-Nov. 1977), 48% showed contamination. The samples were collected from the area bounded by 68°-73°W and 39°30'-40°30'N. The locations of samples containing oil and/or tar from the *Argo* spill area are given in Figure 8. The effect of oil residues on neuston is not clear. However, it has been established that oil can be toxic to clupeid larvae (Kuhnhold, 1977). The larvae of *Ammodytes* and other clupeids continue to be exposed to petroleum hydrocarbons as important constituents of the neuston.

Long-Term Assessment. The grounding and breaking of the *Argo Merchant* and subsequent groundings of other oil tankers on the Continental Shelf are dramatically illustrative of specific events that are not predictable. For example, the Northeast Fisheries Center is frequently requested by responsible officials--local, state, and Federal--to assess the impact of major environmental incidents on the fishery resources of the northeast Continental Shelf. To deal with these incidents special studies are initiated to assess the impact on the environment and living resources. These efforts, however, are of limited duration, and conducted with little information on

Table 3b. Abundance of Fish Larvae per Sample Collected in the Area of the *Argo Merchant* Oil Spill, 4-10 January 1977.

Station	*Ammodytes americanus* (Sand launce)	*Scophthalmus aquosus* (Windowpane)	*Pollachius virens* (Pollock)	*Gadus morhua* (Cod)	*Urophycis sp.* (Hake)	*Clupea harengus* (Herring)	*Gasterosteus aculeatus* (Stickleback)	*Gadidae* (Codfish)	*Enchelyopus cimbrius* (Rockling)
1	4,088	1	1	0	0	0	0	1	0
2	736	0	9	0	0	0	0	0	0
3	236	0	0	0	2	0	0	4	0
4	116	0	18	0	0	0	0	1	0
5	409	0	30	0	0	2	0	42	0
6	1,372	0	10	1	1	1	0	0	0
7	4,316	0	14	0	0	2	0	2	0
8	434	0	3	0	0	0	0	0	0
9	59	0	0	0	0	0	0	0	0
10	8	0	0	0	0	0	0	0	0
11	11	0	0	0	0	0	0	0	0
12	314	0	4	1	0	0	1	0	0
13	302	0	0	4	0	0	0	0	0
*14	1,333	0	0	0	0	0	0	3	0
15	900	0	1	1	0	2	0	0	0
16	306	0	6	1	0	3	0	0	0
17	348	0	4	0	0	0	0	0	0
18	4	0	0	0	0	0	0	0	0
*19	165	0	0	1	0	0	0	0	0
*20	3	0	0	1	0	0	0	0	0
*21	3	0	0	0	0	0	0	0	0
*22	0	0	0	0	0	0	0	0	0
*23	1	0	0	0	0	0	0	0	0
*24	52	0	0	0	0	0	0	0	0
*25	49	0	0	0	0	0	0	0	0
*26	550	0	1	0	0	0	0	0	0
*27	1,499	0	3	3	0	0	0	4	0
*28	854	0	8	6	0	0	0	0	0
29	6,093	0	1	0	0	0	0	0	0
*30	3,720	0	0	0	0	0	0	8	0
*31	37,952	0	0	0	0	0	0	0	0
*32	16,720	0	5	1	0	0	0	0	0
33	2,165	0	8	0	0	0	0	5	1
*34	1,420	0	23	0	0	0	0	0	0
35	286	0	2	0	0	0	0	0	0
*36	5	0	0	0	0	0	0	0	0
*37	0	0	0	0	0	0	0	0	0
*38	159	0	0	0	0	0	0	0	0
*39	62	0	0	0	0	0	0	0	0

NOTE: Values in the table represent combined totals of larvae from surface and water column samples. They are not standardized for volume of water strained.

*Station was within oil slick border as of 3 January 1977.

the initial physiological condition of the living resources. Only limited information on the baseline conditions or health of the stocks is available. We are dealing with a complex system that requires a combination of short-term tactical observations that can be evaluated against a background of long-term baseline information on the condition and health of fish and shellfish stocks.

In order to effectively deal with these problems an approach is needed that: (1) encompasses the coordination of the short-term assessment studies of various groups and agencies conducted in response to a pollution "event," (2) provides for regionally oriented long-term monitoring of ocean environments and populations, and (3) provides suitable information for interim or near-term policy guidance and decision making. The integrated approach should couple in-depth "process oriented" studies at specific sites with long-term monitoring of the productivity of fish stocks. The Northeast Fisheries Center is attempting to bring together these investigative elements in a program called Ocean Pulse. Ongoing surveys of fish, plankton, benthos, and hydrography off the northeast coast of the U.S. will be augmented by developing a physiological baseline at 20 sites on the Continental Shelf to be systematically monitored during the

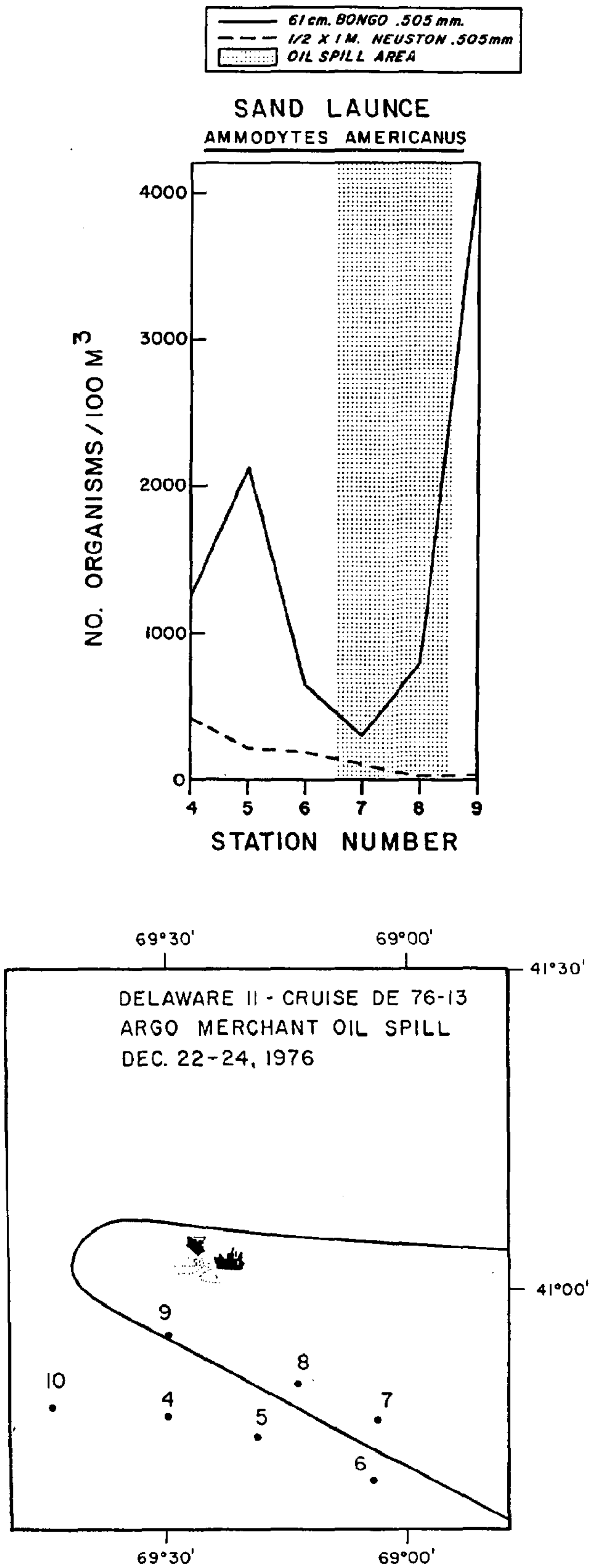

Figure 6. *Numbers of sand launce per 100 m³ collected on Delaware II cruise 76-13 at each of the sampling stations. Stippling designates stations with oil visible in surface waters.*

next several years (Figure 9). The *Argo* spill area represents one of these sites. The principal scientists responsible for developing the diagnostic tests have been designated. During the next six months they will continue to examine physiological conditions among selected samples of key populations collected from the spill area. MARMAP surveys will continue to provide information on changes in the abundance and distribution of stocks and their environments. The Ocean Pulse Program will monitor physiological conditions to detect sublethal or chronic impacts of contaminants on the growth, survival, and productivity of important marine populations. Special attention will be focused on documenting effects that are not readily apparent without biochemical, genetic, and pathological examination at the tissue level. Data collected from clean and contaminated areas will represent baselines against which the impact of oil and other contaminants can be evaluated.

Summary

From the evidence examined, we can conclude that:

(1) The fishery in the vicinity of Nantucket Shoals for the more abundant species (cod, yellowtail flounder, winter flounder and scallops) after the movement of the oil offshore was not adversely affected by the spill. Both the commercial catch statistics and the fisheries independent bottom trawl survey results revealed no downward trends in abundance. Over the broader area encompassing Georges Bank, the results are similar.

(2) Of the fish and shellfish analyzed for petroleum hydrocarbon content, <5% showed any suggestion of *Argo* oil. The suspected oil contamination was limited to the stomachs of 2 cod and 1 windowpane flounder suggesting the oil was ingested.

(3) No adverse effects on fisheries were reported by fishermen. However, it is important to recognize that these observations were limited largely to the less sensitive adult fish, and to a lesser degree to juvenile segments of the populations that are targeted by the fishery.

(4) The sensitive early developmental stages of fish were impacted, as evidenced by the observed mortalities of cod and pollock embryos. However, important environmental factors mitigated the adverse effects on these species: (a) the residence time of the oil over the spawning grounds was minimized by prevailing offshore winds and currents, and (b) the lack of significant amounts of oil detected on the bottom. While some change in the abundance of *Ammodytes* larvae was observed, the species is wide-spread, occurring naturally in "patches." Additional analysis is required to evaluate the level of population change against the expected natural variability in distribution.

(5) Evidence was found of oil entering the food web of Nantucket Shoals. The dominant zooplankter was the copepod *C. typicus.* This species ingested oil particles although no harmful effects on zooplankton have been reported in the literature.

(6) Although the short-term effects of the *Argo* spill were not catastrophic, a proper evaluation of the impact of petroleum hydrocarbons on Continental Shelf populations has yet to be carried out. The *Argo* spill, while spectacular, represents <1% of the total annual input of petroleum hydrocarbons in the World Ocean (NAS 1975). The long-term chronic problem requires far more attention than is presently being directed to its solution.

Table 4. Summary of Hydrocarbon Analyses.

Species	*Cruise*	*Station*[a]	*No. Samples*[b] *Analyzed*	*No. Samples Contaminated*	*Remarks*
Fish					
Cod *(Gadus morhua)*	DE 77-01	3	1	0	
		38	1	1	High degree of correspondence with *Argo Merchant* arkanes in stomach but two orders of magnitude less oil than in special sample from Station 29.
Haddock *(Melanogrammus aeglefinus)*		8	1	0	
		27	1	0	
Silver hake *(Merluccius bilinearis)*		3	1	0	
		24	1	1	Fairly heavy concentration of heavy fuel oil in stomach.
Red hake *(Urophycis chuss)*		10	1	0	
		24	1	0	
Yellowtail flounder *(Limanda ferruginea)*		3	1	0	
		31	1	0	
Winter flounder *(Pseudopleuronectes americanus)*		3	1	1	Moderate concentration of oil in stomach. None in the flesh.
		31	1	1	Heavy concentration of oil in stomach. Lesser concentration in flesh.
Windowpane flounder *(Scophthalmus aquosus)*		3	1	1	Light concentration of oil in the stomach; similar correspondence with *Argo Merchant* or other similar type of fuel oil; no oil in flesh.
	DE 76-13	4	1	0	
Invertebrates					
Sea scallop *(Placopecten magellanicus)*	DE 77-01	3	1	0	
		39	1	0	
Lobster *(Homarus americanus)*	DE 76-13	6	1	0	
	DE 77-01	6	1	1	Slight concentration of oil in flesh.
Sand dollar *(Echinarachinius parma)*	DE 77-01	19	1	0	
		34	1	0	
Special Samples					
Contents of cod stomach containing oil		29	1 (individual)	1	Large amount of oil in stomach; fairly high degree of correspondence with *Argo Merchant* hydrocarbons.
Winter flounder with external smudge of oil	DE 76-13	4	1 (individual)	1	No traces of oil in stomach or flesh.

[a]Figure 7.

[b]Three individuals were pooled to make up one sample.

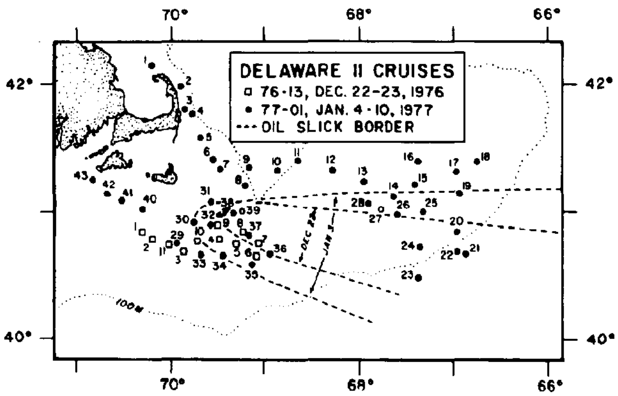

Figure 7. *Station locations of Delaware II 76-13 and 77-01.*

Table 5. Presence of Oil and Tar in Neuston Samples.

Cruise	*Date*	*No. Samples Examined*	*No. Contaminated*	*% Contaminated*	*No. Heavily Contaminated*	*Location of Heavy Contamination*
Researcher 76-01	26 Nov.-12 Dec. 1976	32	2	6	0	
Delaware II 76-13	22-24 December, 1976	5	5	100	5	South and Southeast of *Argo Merchant* wreck
Delaware II 77-01	4-10 January, 1977	38	11	29	4	South and Southeast of *Argo Merchant* wreck
Mt. Mitchell 77-02	12-26 February, 1977	38	21	55	2	Southwest of *Argo Merchant* wreck
Endeavor 005	22-27 Feb.	20	7	35	2	South and Northwest of *Argo Merchant* wreck
Wieczno 77-01	27 Feb.-6 Mar.	41	18	44	4	South and Southeast of *Argo Merchant* wreck
Gorlitz 77-01	3-15 Mar.; 15 Mar.-3 Apr.	22	2	9	0	
Albatross IV 77-02	13 Apr.- 14 May	18	8	44	3	West and Southwest of *Argo Merchant* wreck
Nogliki 77-02	22 May-6 June	34	15	44	2	Northwest of *Argo Merchant* wreck
Yubileiny 77-02	31 Jul.-15 Aug.; 17 Aug.-3 Sept.	33	15	46	5	Three Southwest of the wreck — One East of the wreck and One Northeast of the wreck
Wieczno 77-06	4-24 Oct.	19	11	58	2	Southeast of the wreck
Argus 77-01	15 Oct.-10 Nov.	32	5	16	0	
Total		332	120	36	29	

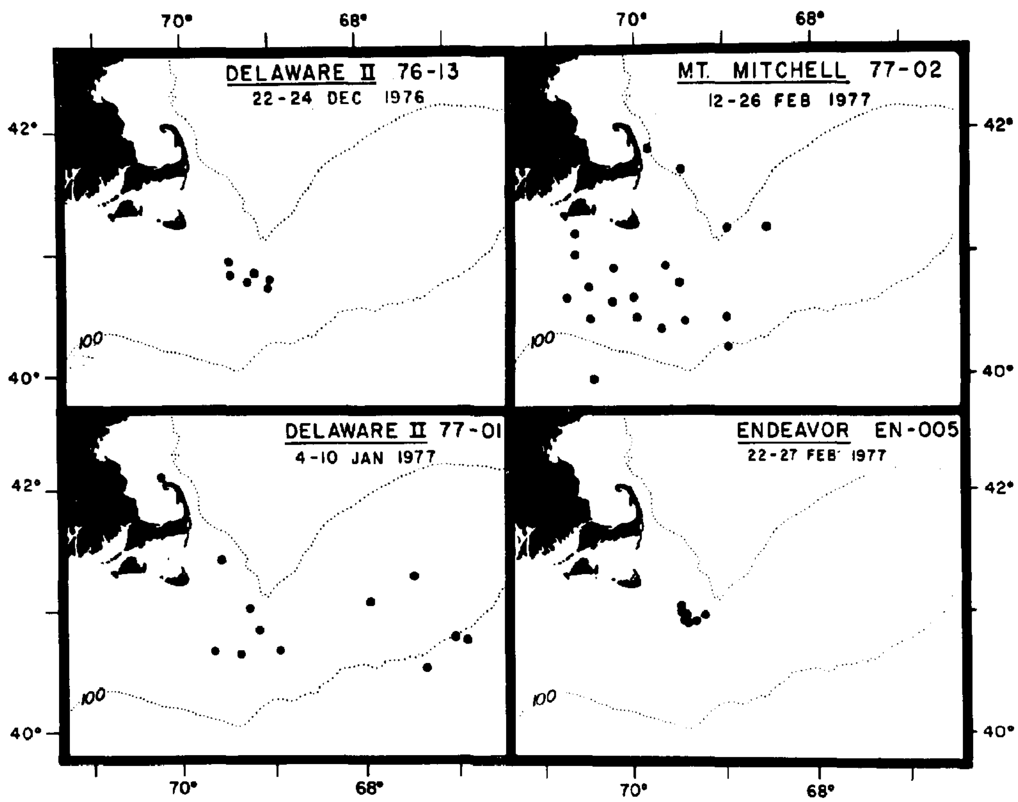

Figure 8a. *Locations of neuston stations in the Argo area where samples contained oil or tar, December 1976-February 1977.*

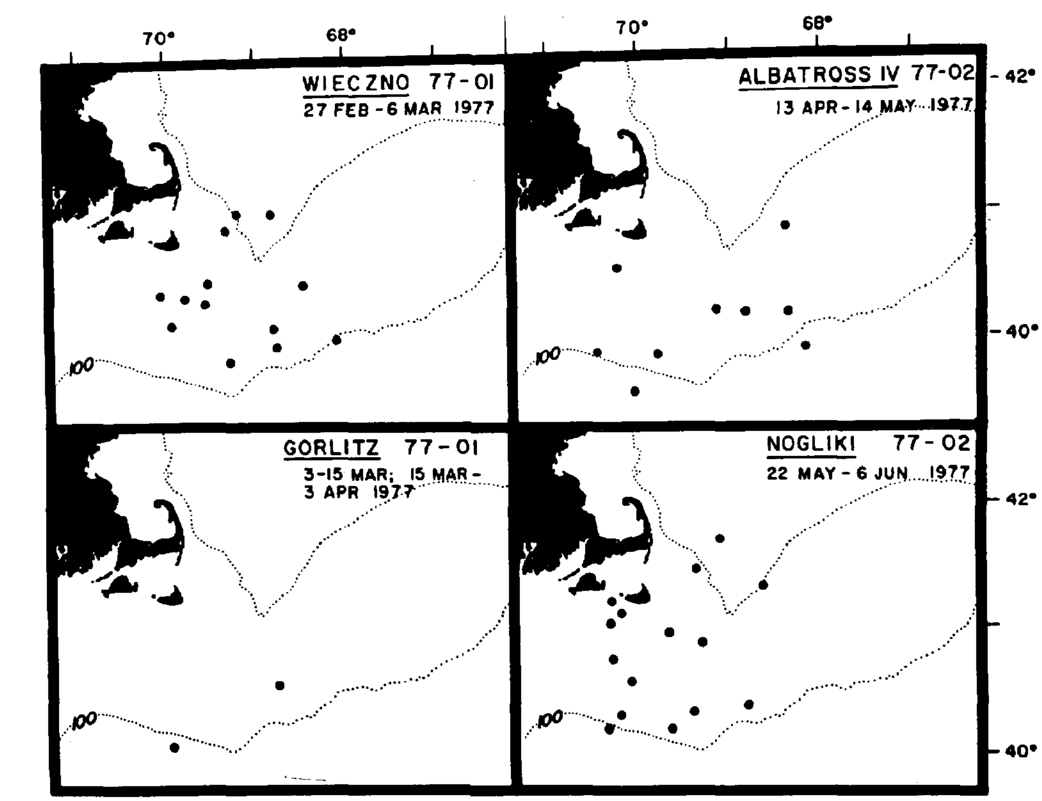

Figure 8b. *Locations of neuston stations in the Argo area where samples contained oil or tar, February 1977-June 1977.*

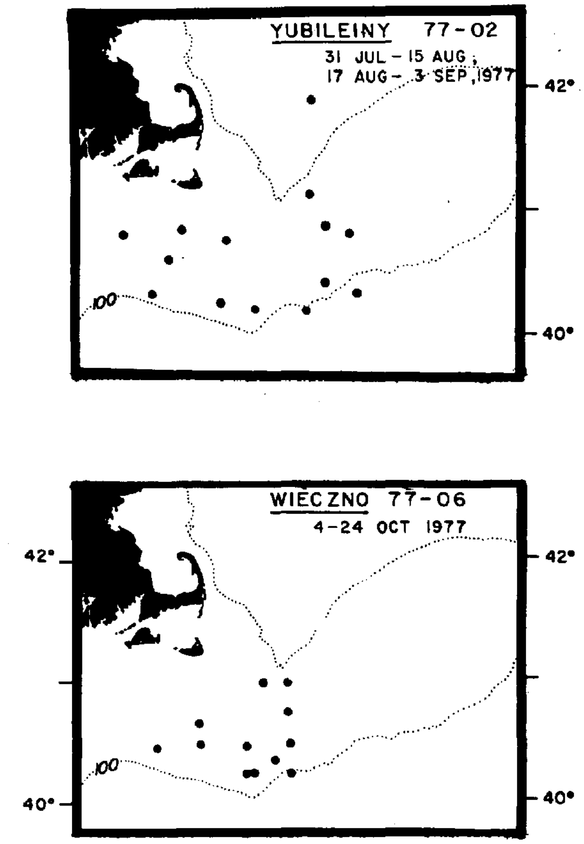

Figure 8c. *Locations of neuston stations in the Argo area where samples contained oil or tar, July 1977-November 1977.*

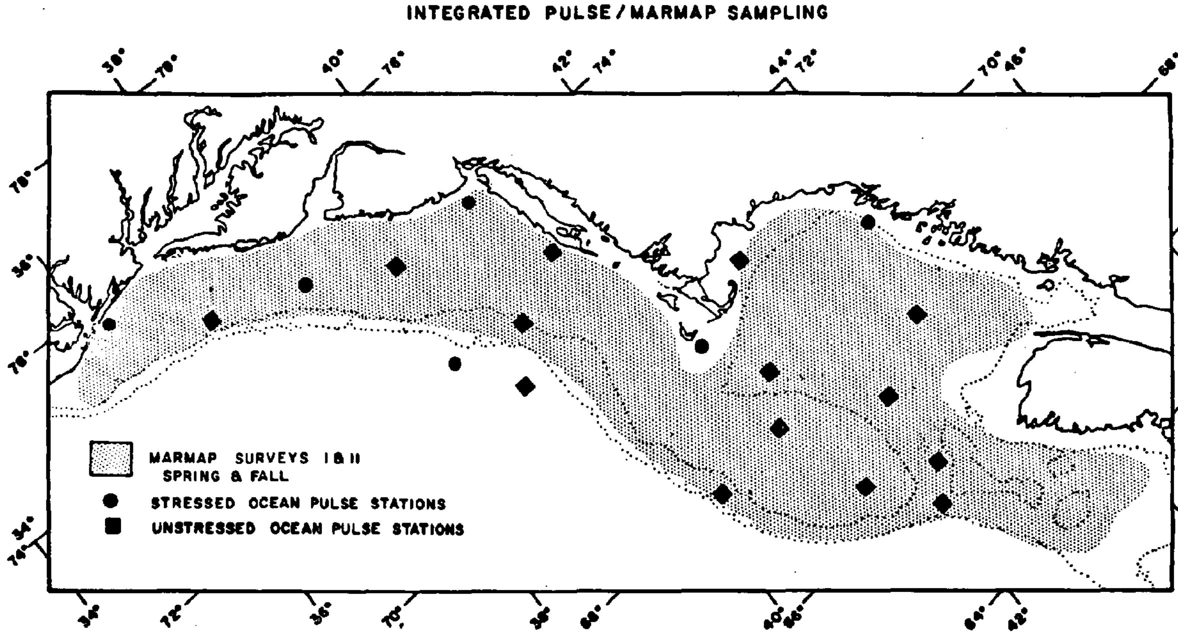

Figure 9. *Integrated Pulse/MARMAP sampling areas off the northeast coast of U.S.*

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Socio-Economic Study

Peter Fricke and John Maiolo

Public Knowledge and Perceptions of the Effects of the *Argo Merchant* Oil Spill

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Thomas and Znaniecki have suggested that if people define a situation as real, it will be real in its consequences (1927). People act on the basis of *perceptions* of situations, even if those perceptions do not square with those of others, or some objective indicator of a situation. As simple as this notion is it has been a powerful tool for social science. Such a notion has assisted in the explanation of conflict, even when the objective conditions would lead one to a prediction of harmony, and vice versa, the analysis of religious behavior, the adoption of new practices and so on.

The research reported in this paper explores the perceptions that residents of Cape Cod, Martha's Vineyard and Nantucket have of the nature and effects of the oil spills that occurred in the area in December 1976, and January 1977. It is felt that knowledge of those perceptions is crucial in understanding the nature of the public response to perceived disasters, as public policies are developed to avert and manage such potential disasters of an environmental nature.

The *Argo Merchant* went aground on the Nantucket Shoals on December 15, 1976. In the ensuing week the tanker broke up and released approximately 27,000 tons of No. 6 residual fuel oil into the North Atlantic. This pollution incident became a major news media event, and radio, television and press coverage was intensive until the New Year (Fricke, ed., 1977). The *Bouchard 65,* a barge carrying a cargo of No. 2 heating oil, grounded on the Cleveland Ledge in Buzzards Bay on January 28, 1977. Approximately 80,000 gallons of oil were released into the Bay at the site of the grounding and off Wings Neck, to which point the barge was taken for cargo transfer operations. At the time of the *Bouchard 65* stranding, Buzzards Bay was extensively covered by ice and the channels to the Cape Cod Canal were being kept open by a U.S. Coast Guard ice-breaking vessel. Initially the *Bouchard 65* oil spill was reported by the regional news media, but soon reports could only be found in the local press.

Both spills were reported by the press as causing widespread ecological damage, which in turn would, it was believed, harm the fishing and tourist industries of the region. Thus an article in the *Christian Science Monitor* reported that the loss of income to fishermen in five Massachusetts towns caused by pollution from the *Argo Merchant* could amount to $27.6 million, with a further possible loss of $83 million to fish processing and marketing companies *(Christian Science Monitor,* December 23, 1976). Fortunately, none of the oil spilled by the *Argo Merchant* appears to have drifted ashore, and the cost of the response to the accident is estimated at $2.7 million to date (Adams, 1977). This does not include the costs of any possible damage to the fishery, since this cannot be determined until statistics for the 1977 year-class of fish are gathered by the National Marine Fisheries Service in the next two or three years. It is possible that even when fishery statistics are available, it will be difficult to isolate precisely the impact of the *Argo Merchant* and *Bouchard 65* oil spills from the effects of the extremely cold winter and spring of 1976-1977 *(Valley Advocate,* January 5, 1977; *Cape Codder,* January 6, 1977; *Falmouth Enterprise,* January 7, 1977; Grose and Mattson, 1977).

The *Bouchard 65* oil spill had an immediate effect, which was widely reported in the local press, in that the

Table 1. Passengers Carried by the Woods Hole, Martha's Vineyard and Nantucket Steamship Authority Between Cape Cod and the Islands*

	1972		*1973*		*1974*		*1975*		*1976*		*1977*	
	No.	*%†*	*No.*	*%†*	*No.*	*%†*	*No.*	*%†*	*No.*	*%†*	*No.*	*%†*
January	23,328	100	27,063	116	25,879	111	28,231	121	28,594	123	22,956	98
February	22,205	100	27,803	125	24,343	110	29,574	133	35,044	158	26,299	118
March	30,360	100	36,878	122	36,919	122	40,947	135	37,591	124	36,011	119
April	52,655	100	63,483	121	61,300	116	57,553	109	73,139	139	72,666	138
May	77,999	100	82,267	106	90,428	116	100,039	128	104,220	134	117,790	151
June	125,414	100	133,479	106	133,759	107	154,731	123	156,803	125	160,371	128
July	220,638	100	213,085	97	226,608	103	263,809	120	258,988	117	298,893	135
August	260,421	100	265,326	102	279,059	107	312,548	120	292,025	112	329,170	126
September	128,997	100	145,969	113	132,064	102	144,896	112	157,570	122	169,185	131
Totals	942,017	100	995,353	106	1,010,359	107	1,132,328	120	1,143,974	121	1,233,341	131

*Statistics supplied by the Woods Hole, Martha's Vineyard and Nantucket Steamship Authority.
†% of traffic carried in 1972.

Table 2. Expenditure by Travellers to Cape Cod, Martha's Vineyard and Nantucket in Dollars[1]

1975		*Cape Cod**	*Martha's Vineyard***	*Nantucket*	*Total for region*
	Winter	37090	840	811	38741
	Spring	77023	3543	3136	83702
	Summer	147262	10155	6483	163900
	Fall	50811	1928	1791	54530
1975	Total	312186	16466	12221	340873
1976					
	Winter	29323	724	918	30965
	Spring	65479	3888	3864	73231
	Summer	143739	9830	8105	161674
	Fall	32212	1746	1582	35540
1976	Total	270753	16188	14469	301410

*Barnstable County **Dukes County

[1] Information from N.G. Cournoyer and J.K. Kindahl, *Travel and Tourism in Massachusetts, 1976.* University of Massachusetts, Amherst. 1977.

shellfish beds in the north-eastern section of Buzzards Bay were closed to the public. Buzzards Bay has suffered from previous spills, and the area has a recent history of closed shellfish beds (Blumer et al., 1970). In addition, the *Bouchard 65* oil impinged more directly on the property of local residents, since the clean-up operations were conducted from various points along the shoreline (Schwob, 1977).

After the initial "crisis" coverage of the oil spill incidents by the press, news items commonly moved to a second phase of reporting. This phase, which we term "editorial," discussed, in comment columns and leaders, the response to the spill and measures that were necessary to either improve the response or avert spills. In the case of the *Argo Merchant* this phase lasted for most of January, i.e. for approximately four weeks after the crisis phase of reporting had ended. The *Bouchard 65* incident attracted less attention, and the crisis phase was over by 10 February and the editorial phase by 20 February. The third phase of reporting consisted of other items which also referred to the spills or brief items concerning continuing research, legislation or action related to the spills. Throughout the period covered by the survey of local newspapers carried out for this study, from January to September 1977, third-phase news stories were published. The proportion declined from 48% of all marine-related news items in January to 12% in September in the *Falmouth Enterprise,* for example. It should be noted that editorial phase articles also appeared when new legislation was prepared (May), congressional hearings were held (August), and when books and reports were published (April and August) which bore on the spills.

From the above it would appear that the reading public, at least, had a variety of information being presented throughout the period up to the study of attitudes carried out in October and November. Television and radio, by nature of their medium, tend to rely on the dramatic image and immediate coverage of events. Thus the grounding of the *Argo Merchant* provided dramatic viewing while the vessel was still above water, and little drama afterward. The *Bouchard 65* spill was not a dramatic incident; a huddle of tugs, barges, Coast Guard buoy tenders and a lot of ice were all there was to see on the television screen for the two days the barge remained off Wings Neck.

There were two fears articulated in conversations with Cape and Island residents and reported in the press at the time of the two spills. First, that the oil spilled would damage the ecology and environment that the residents enjoyed. Second, there was the fear that the publicity given by the news media would harm the fishing and tourist industries. An expression of this concern was shown in the reports in the *Boston Globe* and *Christian Science Monitor* on 23 December that the possible losses computed by Massachusetts' officials for the fishing and tourist industries were of the order of $158 million in 1977. On the same day a report appeared in the *Daily Hampshire Gazette* of a news conference by Dr. Evelyn Murphy, Massachusetts Secretary for Environmental Affairs, in which the setting up of a system of inspection for possible oil contamination of fish was announced. At the same press briefing spokesmen for the fishing industry assured consumers that fish available in the shops were not contaminated by oil.

In addition to the press coverage, information was received by the residents through other channels. The Audubon Society, for example, mailed a circular letter to many residents of the Cape and Islands expressing concern about the impacts of spilled oil on the environment. The Sierra Club also contacted residents for the same purpose. Congressman Gerry Studds sends a quarterly *Report to the People* to all postal patrons in the 12th Congressional District in Massachusetts. In 1977, the issues of this document emphasized his concern about flags of convenience, U.S. Coast Guard capabilities at times of oil spills, and the need for compensation for damage caused by oil pollution. We concluded, then, that information concerning oil spills was readily available to any resident who wished to understand their nature, effects and impacts.

Tourism, and the service industries associated with it, is big business on the Cape and Islands (see Table 1). It is estimated that 75 to 80% of the overall economy of the region is directly attributable to travellers – seasonal homeowners, businessmen, and tourists – as they move about and stay in the Cape Cod region (Cournoyer and Kindahl, 1977). As can be seen in Table 2, visitors to the region spent nearly $341 million in 1975, and over $301 million in 1976, on lodgings and services. The drop in expenditures by travellers in 1976 is attributed by businessmen and officials of their organizations to bicentennial activities elsewhere in the United States which attracted both seasonal residents and tourists. This is reflected in Table 2, which shows the number of passengers carried by the Woods Hole, Martha's Vineyard and Nantucket Steamship Authority ferries. In 1977, however, the number of passengers carried is significantly higher than in 1975 and 1976. Hoteliers and other businessmen reported in interviews that the 1977 season was as good as or better than that of 1975 in terms of both volume of trade and in income earned.

Although the annual summary prepared for the State of Massachusetts by the University of Massachusetts on travel and tourism is not yet available, it would appear from press reports of beach use and participation in other recreational activities, such as the recreational fishing contests, that 1977 has been a good year for the tourist and travel industry. A word of caution should be injected here, however; nearly all the businessmen interviewed agreed that if either the oil from the *Argo Merchant* spill had come ashore or there had been a spill in the late spring or early summer, the impact upon tourism would probably have been great.

The fishing industry on Cape Cod and the Islands is a complex one, but characterized by coastal and near-shore fishing efforts. The vessels used are relatively small and the longest trips made are of the order of a week. The fishing effort is directed toward both shellfish and fin-fish, and the fish caught are landed at the large centers, Nantucket, Edgartown, Chatham, Provincetown and New Bedford. Since fishermen frequently land fish at ports other than their homeport, it is difficult to distinguish clearly the impact an oil spill occurring offshore would have on a particular community. The fishermen can, if a particular fishing area is closed because of oil slicks, shift his efforts elsewhere unless he is tied to the exploitation of a certain species in a specific area.

Massachusetts' Commercial Fisheries by Landings and Value*

	1975	**1976**
Landings (in '000 lbs)	269,952	288,518
Value (in '000 $)	78,470	97,605

*Information from National Marine Fisheries Service, Fisheries of the United States: 1976. U.S. Department of Commerce/National Oceanic and Atmospheric Administration, Washington, D.C. 1977.

Although the press had reported the possibility of a major loss of income to fishermen due to the *Argo Merchant* oil spill, the fishermen interviewed in the course of this study reported that the 1977 season was as good or better than the 1976 season for both catch and earnings. Of the three cases in which it was reported that the spill had affected earnings, these had been temporary losses and were recouped later in the season. The loss of income in each of the three cases was due to the closure of the area around the slick by the U.S. Coast Guard and the consequent inability of the fishermen to haul lobster pots.

Recreational fishing is also an important use of the seas around Cape Cod and the Islands. It is estimated by the National Marine Fisheries Service, in their annual review, Fisheries of the United States: 1976, that some 626,000 households in Massachusetts engage in recreational marine fishing each year. This is the equivalent of 1,300,000 persons approximately. As can be seen in Table 3, many others from nearby states also fish in Massachusetts waters. Again, interviews with the 102 recreational fishermen in our sample indicated that there was no drop in catch which could be attributed to the *Argo Merchant* accident. The 1977 period was seen as good as or better than previous years by three-quarters of the recreational fishermen. Also interviewed in the study were seven owners of bait and tackle shops, who also reported that their businesses did well in 1977. Their previous best year had been 1975, and all charac-

Table 3. Estimated Number of People Participating in Marine Recreational Fishing in Massachusetts by Northeastern State of Residence, June, 1973 – June, 1974*

Connecticut	94,000
Delaware	5,000
Washington, D.C.	2,000
Maine	7,000
Maryland	16,000
Massachusetts	1,300,000
New Hampshire	36,000
New Jersey	98,000
New York	271,000
Pennsylvania	83,000
Rhode Island	61,000
Vermont	10,000
Virginia	14,000
West Virginia	3,000
TOTAL	1,998,000

*Information from *Fisheries of the U.S., 1976.* U.S. Dept of Commerce, NOAA/NMFS, Washington, D.C. 1977.

terized 1977 as surpassing 1975 for volume of tackle sales and rental.

As can be seen from the review of the tourist and fishing industries above it would appear that the effects of the *Argo Merchant* oil spill on the economy of Cape Cod and the Islands were negligible. The published scientific studies of the *Argo Merchant* incident carried out to date also appear to show that impact of the spill upon the environment was negligible. In this study we were interested in the knowledge that the residents of the region had of the impact of the spill and their perceptions, if any, of the effects upon their communities and their own activities. To this end 260 residents of Chatham, Edgartown, Falmouth and Nantucket were interviewed during October and November 1977. In addition, a special subsample of 48 business people were also interviewed in depth to obtain information about economic activities in the region. Both samples were selected at random and can, we believe, be considered representative of the communities from which they were drawn.

The sample population of 260 selected for the perception study had a modal age of 39 years and a mean age of 51 years. Their period of residence in the area ranged from one year to more than 50 years, with a mode of 8 years and a mean of 15 years. This reflects the population growth, largely through in-migration, in the past two decades. The population of Barnstable County, 126,481 in the state census of 1975, has doubled in twenty years. These migrants are well educated (modal number of years of education is 12 while the mean is 13 years) and in "white-collar" and professional occupations. In fact 25% of the sample were the owners of small businesses or in business for themselves. Again, this reflects the service sector of an economy dominated by travel and tourism. Skilled "blue-collar" workers formed 10% of the sample, and another 10% were unskilled workers. Approximately 14% of the sample were retired persons, but again, this brought into focus another anomaly of this region; many respondents who were gainfully employed had retired from jobs in other parts of the United States and had come to live in the Cape Cod region where they had established themselves in small businesses or were working part-time for others. A retired person in our sample was one who was not engaged in any form of work or occupation.

Again the characteristics of the region exerted themselves in the proportion of persons who defined their occupation as marine-related, i.e. their job existed because of the proximity of, and access to, the ocean. Many of these respondents were in the tourist industry, and in all they constituted about one-fifth of the sample.

Percentage of Respondents Who Define Their Occupations As Marine-related By Community

Chatham	Edgartown	Falmouth	Nantucket	All
21%	15%	19%	29%	18%

The proximity to the ocean is reflected also in recreational activities, such as swimming, boating and fishing. During the summer months two-thirds of the sample engaged in these pastimes, and 11% continued to do so in the winter as well.

The respondents also utilized the mass media to a large extent. Thus 87% of the sample reported that they watched television for at least one hour every day, 89% read a newspaper for at least an hour a day, and 73% listened to the radio for more than an hour a day. The indications were, therefore, that the sample would be well-informed and concerned about the nature and effects of oil spills. The interviewers sought to verify this.

In order to assess the quality of the knowledge of respondents a scale was constructed on which the depth of information could be measured. The researchers labelled the respondents *well informed* if they were able to identify two major polluters, and the location of the incidents, in the area during the winter 1976-77. Thus it was expected that a well-informed respondent would know of the *Argo Merchant* and the *Bouchard 65* accidents, and possibly would be able to name other incidents as well. Persons knowing of one of the two vessels and its location were labelled *informed;* persons knowing either of one of the two ships or of one of the two locations were labelled *poorly informed.* Persons not able to recall any information were labelled *uninformed.* As it turned out this scale had to be collapsed to the categories of informed and poorly-informed/uninformed, because only 14% of the sample could be considered well-informed, and 17% met our criteria for informed respondents. Fully 69% of the sample were badly informed or had no knowledge (or recall) of the two major spills that occurred in the area eleven months prior to the interviews. (See Table 4.)

The respondents were asked to name the organization or agency which had the responsibility for ensuring that spilled oil was cleaned up. For coastal oil spills, such as those of the *Argo Merchant* and *Bouchard 65,* the Coast Guard is responsible for clean up and it was expected that well-informed and informed respondents would know

Table 4. Knowledge of the *Argo Merchant* and *Bouchard 65* Oil Spills by Community (%)

Level of Knowledge	*Chatham*	*Edgartown*	*Falmouth*	*Nantucket*	*Total*
Informed	29	25	45	23	31
Poorly informed/ uninformed	71	75	55	77	69

Table 5. Comparison of Informed and Poorly Informed/Uninformed Respondents' Knowledge Regarding Responsibility for Oil Spill Clean Up (%)

Responsible Organization	*Informed group*	*Poorly informed/ uninformed group*
U.S. Coast Guard	54	47
Coast Guard and other agencies	20	8
Other	15	23
Don't Know	11	38

Table 6. Knowledge of *Argo Merchant* Spill Effects Reported by Respondents by Source of Information and Community (N.B. multiple sources of information could be, and were, given)

Source	*Community**			
	Chatham	*Edgartown*	*Falmouth*	*Nantucket*
T.V.	56	31	61	39
Radio	49	28	37	26
Newspapers	49	68	74	12
Friends	7	37	23	38

*Magazines, relatives and other excluded because of small number of responses.

this. The results are shown in Table 5, and indicate that nearly three-quarters (74%) of the informed group believed that the Coast Guard had some or all of the responsibility for oil spill clean up. Fifty-five percent of the poorly informed/uninformed group of respondents believed that the Coast Guard had some or all of the responsibility, while 23% named other agencies and 38% did not know who was responsible.

Information about the *Argo Merchant* oil spill was obtained from television programs by 65% of the sample. In addition, 53% of the respondents reported that they obtained information from newspapers, and 42% also heard news stories about the spill on the radio. Relatives were an additional source of information for 5% of the respondents, and friends for 18%. Over three-quarters (76%) of the persons interviewed said that they "knew" of some of the effects of the *Argo Merchant* spill, and here differences were found by community. Ninety-five percent of the residents of Falmouth who were interviewed said they "knew" of effects. In Edgartown, 82% of the sample "knew" of effects, in Nantucket, 59%, and in Chatham, 52%. Newspapers were found to be the most frequently cited source of such knowledge (53%), followed by television (47%), and radio (33%). (See Table 6.)

The respondents were asked if they had actually seen or experienced effects of the *Argo Merchant* oil spill, and 45% of all the sample said they had seen effects. Thirty-four percent of the whole sample reported that their lives had been affected in some way, but only 5% reported that specific *activities* had been affected by the oil spill. Of those who reported experiencing effects (34% of the whole sample) it was found that the reported effects were "presumed" to be effects, but at best were indirect. For example, the increased price of shellfish was attributed to the *Argo Merchant* spill, as was the rising cost of fuel oil. Some respondents reported that the knowledge that birds and fish were being affected by the spill distressed them, and as such this was an effect of the incident. (See Table 7.)

When comparison was made of the perceptions of the informed group with those of the poorly-informed/uninformed group concerning the effects of the wreck of the *Argo Merchant* it was somewhat surprising to the researchers to discover that the informed group indicated that they had perceived greater effects than the other group (see Table 8). However, of those who reported that a specific activity had been affected, there was no difference between groups. It should be noted here that of those who reported that the *Argo Merchant* oil spill affected a specific activity, two of the respondents were fishermen unable to reach the lobster fishing grounds because the oil slick lay in their path, and a third respondent was a fish merchant whose supply of lobsters had been curtailed because of restrictions placed on vessels fishing near the slick. The other respondents either had to undertake work directly connected with the spill or had benefited from increased demand for travel and tourist services created by the influx of personnel associated in some way with the spill.

When the sources of information utilized by the "knowledge" groupings of respondents were analyzed few differences were found, with one exception. Fewer informed respondents (20%) indicated that friends and/or relatives were a source of information than the other group (32%). (See Table 9.)

Included in this random sample of 260 residents of the Cape and Islands were 65 owners of businesses. Of these, 35 (54%) reported that their trade was seasonal, i.e. was tourist oriented. As was expected the percentage differed by community, viz. 82% in Edgartown, 64% in Chatham, 50% in Nantucket, and 38% in Falmouth. All had

Table 7. Perceived Effects of the *Argo Merchant* Oil Spill by Community (%)

	Chatham	*Edgartown*	*Falmouth*	*Nantucket*	*Sample*
Reported seeing effects	23	74 74	53	38	45
Reported affecting respondent	16	43	49	25	34
Reported specific activities affected	*	*	*	*	5%

*Number of responses too small to compare by community.

Table 8. Comparison of Perceived Effects of the *Argo Merchant* Oil Spill Reported by Informed and Poorly Informed/Uninformed Respondents (% of group)

Perception	*Informed Group*	*Poorly informed/ uninformed Group*
Reported seeing an effect	49	39
Reported affecting respondent	38	33
Reported specific activity affected	5	5

Table 9. Comparison of Sources of Information About the *Argo Merchant* Oil Spill Between Informed and Poorly Informed/ Uninformed Respondents (% of group)

Source	*Informed group*	*Poorly informed/ uninformed group*
T.V.	46	46
Radio	33	31
Newspapers	53	52
Magazines	12	7
Friends/Relatives	20	32

felt concerned that the *Argo Merchant's* mishap would adversely affect their summer season because of the weight of publicity in December 1976. However, 60% of the business owners felt that the summer of 1977 had brought the normal number of tourists to their region. Forty percent of the owners felt that a change had occurred, and of these, three-quarters said that their trade and the number of tourists had increased. Of all the proprietors, 92% felt their business in 1977 was the same as (60%) or better (32%) than previous years.

Attention was also directed at those respondents who enjoyed fishing as a pastime. Of this sub-sample of 102 respondents, 58% indicated that they owned a boat (alone or with a partner). Nearly three-quarters of the recreational fishermen perceived the 1977 fishing season as being the same or better than previous years. Of those who indicated that fishing was worse, many commented that "natural" cyclical factors were operating. Oil spills were not blamed for poor catches, with the exception of those respondents seeking shellfish in Vineyard Sound, and spills prior to the *Argo Merchant* were said to have damaged this fishery.

To summarize, of the sample of 260 residents of Cape Cod, Martha's Vineyard and Nantucket, interviewed about their knowledge and perceptions of the effects of the *Argo Merchant* oil spill, 69% were either poorly informed or uninformed (or had no recall) of the events of the winter of 1976-77. An operating assumption of the study was that if basic information was unknown, more detailed knowledge of the extent of oil spills, environmental damage and pollution clean-up would also be unknown. It can be fairly said that an uninformed public is a susceptible one in that impressions, incomplete reports and informal sources of information can appreciably affect public opinion to the extent that a large gap exists between perceptions and reality.

The three major sources of information utilized by the respondents were television, newspapers and radio. If our index of knowledge is accepted, these media functioned to inform and keep informed less than a third of the sample. Yet three-quarters of the sample said they "knew" of effects of the *Argo Merchant* oil spill and 45% reported that they had "seen" effects, most of which were environmental. An inspection of the data obtained by in-depth questioning by interviewers reveals that these "observed" effects were taken seriously by the respondents. The perceptions of the situation for those respondents, whether or not those perceptions square with reality, are that the *Argo Merchant* oil spill was damaging to the environment and/or to the social and economic life of the Cape Cod region. It is believed by the authors that knowledge of these perceptions needs to be incorporated into any effects to inform the public and into any planning for the prevention of or response to oil spills.

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Future Response Plans

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Ecological Damage Assessment of Oil Spills–the Federal Government's Response

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The authority for the federal government to respond to spills of oil and hazardous substances stems from the Federal Water Pollution Control Act (FWPCA) Amendments of 1972 (PL 92-500, Section 311) and the 1977 Amendments to the Act (33 U.S.C. 466 et seq.). The applicable regulations are given in the National Oil and Hazardous Substances Pollution Contingency Plan (40 CFR 1510).

The highlights of Section 311 of the FWPCA are as follows:

*Prohibits the discharge of harmful quantities of oil and other hazardous substances to the waters of the U.S.;

*Requires notification to the federal government whenever a prohibited discharge occurs;

*Authorizes the President to remove or arrange for the removal of an oil spill unless such removal is properly carried out by the responsible party;

*Requires the promulgation of a national contingency plan to provide for efficient, coordinated and effective action to minimize damage from oil or hazardous substances spills;

*Establishes liability limits for vessels, onshore facilities and offshore facilities for the costs of removing spills caused by these facilities;

*Authorizes the President to promulgate regulations:
- -establishing methods for removal of oil and hazardous substances spills,
- -governing the inspection of vessels carrying oil and hazardous substances cargos,
- -establishing criteria for the development and implementation of local and regional contingency plans for spill removal, and
- -establishing procedures and methods for preventing discharges of oil and hazardous substances from vessels, onshore facilities and offshore facilities;

*Authorizes the establishment of a revolving fund to pay for the cost of oil and hazardous substances spill removal;

*Establishes a system of enforcement and provides for penalties for violation of any part of Section 311;

*Assigns responsibility for various aspects of oil spill response among federal agencies;

*Establishes a national response team to oversee the federal government's involvement in oil spills, composed of five primary federal agencies (DOT, DOI, DOD, EPA, DOC) and a number of advisory agencies;

*Establishes mechanisms to coordinate all oil spill response through a single federal agent - the "On-Scene Coordinator;"

*Establishes a schedule to regulate the use of chemicals and other additives to remove oil and hazardous substances discharge.

The National Contingency Plan (NCP) identifies five federal agencies for primary responsibility in dealing with oil and hazardous substances spills. The primary agencies and their responsibilities are as follows:

1. Department of Transportation (DOT)

*Provide expertise in port safety and security, marine law enforcement, navigation and construction, manning, operation and safety of vessels;

*Furnish or provide for the On-Scene Coordinator (OSC) for coastal waters and the Great Lakes;

*Chair RRT in areas where it provides OSC;

*Develop, implement and revise regional contingency plans in areas where it provides OSC.

2. Department of the Interior (DOI)

*Provide expertise in oil drilling; producing, handling and pipeline transportation;

*Through its regional coordinators, provide technical expertise to the OSC and RRT with respect to land, fish and wildlife, and other resources for which it is responsible;

*In conjunction with state liaison to RRT arrange for and coordinate actions of groups to establish bird collection, cleaning and recovery centers.

3. Department of Defense (DOD)

*Provide assistance in critical pollution discharges, consistent with its operational requirements;

*Provide assistance in the maintenance of navigation channels, salvage, and removal of navigation obstructions.

4. Department of Commerce (DOC)

*Through NOAA, provide support to the NRT, RRT and OSC with respect to marine environmental data, living marine resources, current and predicted meteorological, hydrologic and oceanographic conditions for the high seas, coastal and inland waters;

*Provide maps and charts, including tides and currents for coastal and territorial waters, and the Great Lakes;

*Through MARAD, provide advice on the design, construction and operation of merchant ships.

5. Environmental Protection Agency (EPA)

*Provide expertise regarding:
- -environmental effects of pollution discharges
- -environmental pollution control techniques
- -assessment of damages;

*Provide advice to the RRT and OSC of the degree of hazard a particular discharge poses to the public health or welfare;

*Furnish or provide for the OSC for inland waters;

*Chair RRT for areas in which it provides the OSC;

*Develop, implement and revise regional contingency plans for areas where it provides the OSC;

*Provide guidance to and coordinate with DOT regarding pollution control and protection of the environment in the preparation of regional plans.

It is important to note that the U.S. Coast Guard provides the OSC for spills occurring in coastal waters (extending inland to the extent of tidal influence) and the Great Lakes. The U.S. Environmental Protection Agency (EPA) provides the OSC for all other waters of the United States and its possessions, i.e., essentially all fresh water spills. In carrying out his function the OSC has broad authority to take whatever steps are necessary to ensure a timely and effective clean-up operation. The OSC uses as guidance existing regional and local spill contingency plans. He can receive advice and assistance from both the Regional Response Team (RRT) and the National Response Team (NRT). The OSC has at his disposal a spill contingency fund which he can use at his discretion to pay the costs of the clean-up operation.

Under the terms of the NCP, the EPA is assigned the responsibility for determining the extent of damage resulting from major spills. Funding for damage assessment studies can not be obtained from the present spill contingency fund. Nevertheless, 19 studies of spills have been performed using EPA funding sources.

The *Argo Merchant* spill revealed that in carrying out a large damage assessment study, many areas, such as coordination of studies, planning for studies, and the state of the art in performing studies, were less than desirable. In the spring of 1977 the National Response Team moved to improve its capabilities for performing assessments of damage, especially ecological damage, by establishing an ad hoc inter-agency task force to examine the problem of damage assessment and report back to the NRT their recommendations.

The objectives of the task force were to provide a plan of action which would enable the federal government to:
- -provide highly qualified and coordinated scientific support to regional response teams and on-scene coordinators during major spill incidents;
- -upgrade our capability to assess environmental damage associated with these spills; and
- -capitalize on the unique research opportunities which are often afforded by major spills and thus improve our ability to support future clean-up and damage assessment activities.

The task force concluded:
- -although a great deal of scientific capability exists at present to provide assistance to those involved in clean-up, damage assessment and public information activities, we are not now prepared to provide that support on a routine basis;
- -future efforts must be organized in a manner which will allow a prompt match of scientific capability to the issues involved in operations and assessment; and
- -the research base is currently inadequate to resolve many of the questions raised by such spills.

The task force arrived at the following recommendations to the National Response Team:
- -establishment of a national scientific support coordinator as part of the NRT;
- -establishment of scientific support coordinators (SSC) on either a regional or an area basis, the coordinator to serve as the single contact with the OSC for all environmental inputs/issues;
- -development of scientific support teams to function under the SSC as an operational arm of the regional response team; and
- -development of regional contingency plans for ecological assessment through a series of workshops to be held in each EPA coastal region.

The first regional workshop was held for New England (EPA, Region 1) August 28-31, 1977, in Hartford, Connecticut. Based on the workshop, specific plans for performing ecological damage assessments of major oil spills are being formulated.

The second workshop was held in Anchorage, Alaska on November 28-30, 1977, to assist in developing a plan specific to the needs of Alaska.

The third workshop, for the entire Gulf of Mexico, was held April 3-5, 1978, in Tampa, Florida.

The objectives of the workshops are:

*To identify experts presently working in oil pollution research and operations in the region;

*To compile research needs and projects applicable to the environmental characteristics of the region which could comprise elements of damage assessment studies or research programs;

*To catalogue identified experts and their areas of expertise into a regional directory of oil spill workers who could be called on for scientific advice to the On-Scene Coordinator during spill incidents;

*To identify presently available resources, facilities, and support services for scientific responses to oil spills.

The emergency response for damage assessment studies focuses on using local scientific resources supplemented by national expertise and capability in specialized areas such as analytical chemistry and spill trajectory analysis. The planned field programs will be under the direction of the Scientific Support Coordinator (SSC). The national plan identifies two SSC's for each coastal area — one from EPA for spills originating inside the baseline from which the territorial sea is measured (essentially spills in bays, estuaries, rivers, etc.) and a SSC from NOAA responsible for spills originating outside the baseline (such as the *Argo Merchant* spill).

Pending legislation dealing with the so-called "superfund" would provide, if passed, a $200,000,000 liability fund. The unique feature of this legislation from an ecological science perspective is the provision allowing for compensation for damages to "natural resources". Clearly, if this legislation passes, the marine science community will be tasked with defining "damage" to "natural resources" and perfecting the methodology to allow the use of scientific information in economic/legal evaluations. The federal program briefly described above is an attempt to come to grips with this challenging problem and in the process develop a framework for most effectively using scarce resources to learn what is the true extent of damage resulting from spills of oil and hazardous substances.

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